
SOURCE APPORTIONMENT AND CHEMICAL CHARACTERISATION OF AIRBORNE FINE PARTICULATE MATTER IN CHRISTCHURCH, NEW ZEALAND

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**by
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Eclogue: Christchurch in Winter

*Ultima Cumaei venit iam carminis aetas:
magnus ab entegro saeculorum nascitu ordo.*
Vergil, Eclogue IV

In Te Wai Pounamu, winter comes in hard
straight off the Antarctic ice floes, scything low
over the flat scrub of the plains & outside
the sheltered harbours Tawhirimatea of the storms
lashes at
Tangaroa's glum lead waters with his fists. In
the wet black sand, the godwits print angelic biographies
with their bird-foot cuneiform before
they take off for the warmer lakes of Siberia

North Hagley Park smokes like an old piece
of roof tin chucked on a tip fire
with the breath of people and bare willows
in this grey steel freezer of a South Island cold snap.
Joggers & dogs towing their people cough up
expanding gypsophila blooms.

Far out, resting on the surface of the nation
of groper, terakihi & the ugly roughy, a Russian
trawler captain looks to an angry black horizon,
dreaming of a bountiful catch.

The office lemming plucks a file from the cabinet,
delicately like Orpheus strumming his lyre. He looks
out into the raw grey day &
moves closer to the radiator.

As soon as afternoon tea is over, darkness falls.
Spring becomes
a bitter aftertaste & talk of cherry blossom
drops out of frequency. The Southerly chooses to whistle
a subzero tune from the Ice Age's greatest hits
until my cheeks burn like beetroot.

The streets are stuccoed, candy-coated –
Jack Frost's crack troops
are parachuting in through a sky dirty white on white:
Scandinavian snipers
in Artic camouflage,
a charcoal picture, the trees are by Mondrian.

This monochrome remains
even after I shut my stinging eyes.

ANDREW PAUL WOOD
From Big Sky, A collection of Canterbury poems

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List of acronyms and abbreviations

Al	Aluminium	K	Potassium
ANSTO	Australian Nuclear Science and Technology Organisation	LPG	Liquid petroleum gas
As	Arsenic	Mg	Magnesium
Ba	Barium	MFE	Ministry for the Environment
BC	Black carbon	MLR	Multiple linear regression
Br	Bromine	Mn	Manganese
Ca	Calcium	MoT	Ministry of Transport
CCC	Christchurch City Council	NES	National Environmental Standard
CCN	Cloud condensation nuclei	Na	Sodium
Cl	Chlorine	Na ₂ SO ₄	Sodium sulphate
CMB	Chemical mass balance	NaCl	Sodium chloride
Co	Cobalt	NaNO ₃	Sodium nitrate
CO	Carbon monoxide	NH ₃	Ammonia
CO ₂	Carbon dioxide	NH ₄ ⁺	Ammonium
Cr	Chromium	NH ₄ NO ₃	Ammonium nitrate
CRC	Canterbury Regional Council	(NH ₄) ₂ SO ₄	Ammonium sulphate
Cu	Copper	NH ₄ HSO ₄	Ammonium bisulphate
DMS	Dimethyl sulphide	Ni	Nickel
EC	Elemental carbon	NIWA	National Institute of Water and Atmospheric Research
EDS	Energy dispersive spectroscopy	NO ₂	Nitrogen dioxide
FA	Factor analysis	NO ₃	Nitrate radical
Fe	Iron	NO ₃ ⁻	Nitrate
Ga	Gallium	NO _x	Oxides of nitrogen
Ge	Germanium	NRRP	Natural Resources Regional Plan
GNS	Institute of Geological and Nuclear Sciences	OC	Organic carbon
H ₂ S	Hydrogen sulphide	OC _{mass}	Organic carbon mass
H ₂ SO ₄	Sulphuric acid	OH	Hydroxyl
Hg	Mercury	P	Phosphorus
HNO ₃	Nitric acid	Pb	Lead
IC	Ion chromatography	PAH	Polycyclic aromatic hydrocarbons
		PCA	Principal components analysis

PIXE	Proton induced x-ray emission	V	Vanadium
PM	Particulate matter	VKT	Vehicle kilometres travelled
PM _{2.5}	Particulate matter less than 2.5 microns in aerodynamic diameter	Y	Yttrium
PM ₁₀	Particulate matter less than 10 microns in aerodynamic diameter	Zn	Zinc
PM _{10-2.5}	Particulate matter between 2.5 and 10 microns in aerodynamic diameter	Zr	Zirconium
PMF	Positive Matrix Factorisation		
R&P	Rupprecht & Patashnick		
Rb	Rubidium		
RMA	Resource Management Act		
RPS	Regional Policy Statement		
S	Sulphur		
SASS	Spiral Aerosol Speciation Sampler		
Sc	Scandium		
SCC	Sharp cutoff cyclone		
Se	Selenium		
SEM	Scanning electron microscopy		
Si	Silicon		
SO ₂	Sulphur dioxide		
SO ₃	Sulphur trioxide		
SO ₄ ²⁻	Sulphate		
SO _x	Oxides of sulphur		
Sr	Strontium		
SuperSASS	Speciation Aerosol Sampling System		
TC	Total carbon		
TC _{mass}	Total carbon mass		
TEOM	Tapered element oscillating microbalance		
Ti	Titanium		
TMO	Thermal manganese dioxide oxidation		
TOR	Thermal/optical reflectance		
TOT	Thermal/optical transmittance		
TSP	Total suspended particulate		
USEPA	United States Environmental Protection Agency		

Abstract

Environment Canterbury has a proposed plan to address elevated wintertime particle concentrations in Christchurch and other Canterbury towns. The proposed plan sets out air quality objectives for Canterbury and specifically targets the main source of wintertime particles, residential heating. Environment Canterbury is reliant on the plan strategies to meet the targets specified, and to meet the recently established National Environmental Standard for PM_{10} . The contribution of residential heating, relative to other sources, has been quantified by emission inventory (coupled with a box model). The appropriateness of measures contained in the proposed plan is debated by some, who are sceptical of the inventory results. Progress in air quality management in Christchurch would be facilitated by improving the understanding of $PM_{2.5}$ and its sources by undertaking an alternative approach to source attribution.

A source apportionment study was therefore conducted during 2001/2002 to address these issues. This aimed to determine the chemical composition of fine particles ($PM_{2.5}$) in Christchurch, investigate and trial a receptor model, identify the main sources contributing to $PM_{2.5}$ and estimate relative source contributions with a view to using the technique to monitor plan strategy effectiveness. This is the first time that the Positive Matrix Factorisation (PMF) receptor model has been applied to seasonal $PM_{2.5}$ data in New Zealand.

$PM_{2.5}$ samples were collected at St Albans, Christchurch during 2001 and 2002. The filters were analysed for gravimetric mass, elemental species and inorganic ions (24-hour averages). Organic and elemental carbon were measured using an automatic carbon analyser. The final dataset comprised 159 observations and 15 chemical species. $PM_{2.5}$ concentrations were seasonally distributed with maximum concentrations occurring in winter. Major elemental constituents were organic and elemental carbon, sulphate, nitrate, sodium, chlorine and sulphur. Combustion-related species were highest in winter and those derived from natural sources (e.g. marine aerosol) predominant in summer. Five factors were resolved using the PMF receptor model: these were identified as wood combustion, marine aerosol, motor vehicles, secondary particulate and aged aerosol. On average, 92% of $PM_{2.5}$ mass was explained by the resolved factors. The most important source of $PM_{2.5}$, on average, during summer was aged aerosol and in winter was wood combustion. The results were evaluated against inventory-derived data; both methods clearly identified wood combustion as being the predominant source of peak wintertime $PM_{2.5}$ (92% and 89%, respectively). These results provide independent verification that residential heating is the greatest contributor to wintertime particles, adding to the "weight of evidence" required to justify strategies adopted in Environment Canterbury's proposed plan. Further use of receptor models was recommended as they provide source information unavailable from emission inventories, including contributions from natural sources and secondary particulate, and may be used to track effectiveness of policy implementation.

Chapter 1: Introduction

The residential population of Christchurch, a city located on the eastern coastline of the South Island of New Zealand, is exposed to elevated pollutant concentrations every winter. Various measures have been introduced over time to control and regulate emissions to air, yet degraded air quality persists. Particulate matter less than 10 microns in size (PM_{10}) is the main pollutant of concern, and as such, air quality monitoring and investigation has focused on this contaminant (Aberkane *et al.*, 2004a,b; Foster, 1998a).

In more recent years, the potential effects of the fine particle fraction ($PM_{2.5}$) on human health has become of greater concern. Scientific evidence suggests that $PM_{2.5}$ may be the size fraction actually responsible for those adverse health effects attributed to PM_{10} , due to its enhanced capacity for respiratory penetration and retention. Greater associations between specific health effects and $PM_{2.5}$ have been reported, than with coarse particles ($PM_{10-2.5}$) (Schwartz *et al.*, 1996; Schwartz and Neas, 2000; Ilabaca *et al.*, 1999; Delfino *et al.*, 1997). The epidemiological evidence is presently inconclusive, but it is generally agreed that fine particles travel more deeply into the lungs and may have greater impacts than PM_{10} .

Monitoring of $PM_{2.5}$ in Christchurch, to date, has been limited to a number of short-term studies. These studies found that fine particles in Christchurch were present at unhealthy levels. Twenty-four hour average $PM_{2.5}$ concentrations, measured during the winter of 2001, for example, frequently exceeded suggested threshold values. A maximum 24-hour average concentration of $143 \mu g m^{-3}$ was reported by Scott (2002), with 39 exceedences of New Zealand's Ministry for the Environment's (MfE) suggested monitoring value of $25 \mu g m^{-3}$. Management intervention is clearly required to maintain a healthy standard of air quality for the local community.

Management of air quality in Christchurch, and wider Canterbury, is the responsibility of the regional authority, Environment Canterbury. Environment Canterbury has monitored and investigated air quality throughout the region and found that health-based guidelines for PM_{10} were regularly exceeded in Christchurch, and other parts of Canterbury, and that the main source of emissions in these areas was residential heating. Although few measurements of $PM_{2.5}$ have been conducted in Christchurch, it has been demonstrated that on days when the PM_{10} guideline is exceeded, approximately 90% of PM_{10} constitutes $PM_{2.5}$ (Foster, 1998a). In response to these concerns, the proposed Canterbury Natural Resources Regional Plan – Air Quality (NRRP) was developed and notified in June 2002.

One of the main objectives of the proposed NRRP is to decrease the number of days when 24-hour average PM_{10} is greater than $50 \mu g m^{-3}$, down to one annual exceedence (averaged over three years) by 2012. In addition, the MfE recently introduced National Environmental Standards (NES) for various contaminants, including PM_{10} . The NES for PM_{10} allows only one annual exceedence of $50 \mu g m^{-3}$ (24-hour average) from 2013. Regional authorities will not be able to issue air discharge resource consents to any activity that may cause concentrations to deviate above a modelled downward trend-line (i.e. go above a "straight line path"). Greater certainty and knowledge of the natural and secondary particulate contributions to PM_{10} will be required, to ensure that primary anthropogenic emissions are sufficiently reduced. Stringent management measures are necessary for attainment of these air quality targets.

The proposed NRRP places strict requirements on discharges to air in Christchurch, and to a lesser extent on activities outside Christchurch. While it imposes restrictions on many types of air discharges, emissions from residential heating are a particular focus. The proposed plan, for example, bans the installation of solid fuel burning appliances into new homes (or homes that do not currently use solid fuel for heating), requires the removal and replacement of solid fuel burners after 15 years of operation, and bans the use of open fires from 2006. To assist in achieving this outcome, an incentives and assistance scheme, known as the Clean Heat Project, was initiated. The incentives programme encourages householders to remove high emission solid fuel burners and replace them with low emission burners or electrical appliances. Consequently, emissions of PM_{10} and $PM_{2.5}$ from residential heating are expected to decline, with corresponding reductions occurring in measured concentrations.

However, the proposed measures targeting residential heating are presently subject to a degree of community resistance. A view perpetuated by some is that residential heating is not the major source of PM_{10} and $PM_{2.5}$, and that motor vehicle emissions are of greater significance than that suggested by Environment Canterbury.¹ This misconception must be addressed, as community support and action is central to the success of the plan strategies. To achieve greater community support, Environment Canterbury needs to demonstrate a robust understanding of local emission sources and their contributions to local air quality issues. Further source attribution work therefore is required to address these concerns and to provide greater confidence that the strategies adopted will achieve substantial reductions in particulate matter (PM) in Christchurch.

The plan is not yet operational as commissioners are presently hearing submissions to the plan. Once the plan is finalised, it will be necessary, over time, to monitor the effectiveness of the management strategies on air quality. Methodologies adopted should have the ability to indicate whether PM_{10} and

¹ For example, the 2002 Christchurch emission inventory suggests that in Metropolitan Christchurch 85% of PM_{10} emissions originate from residential heating, 9% from motor vehicles and 6% from industrial/commercial sources (Scott and Gunatilaka, 2004).

PM_{2.5} concentrations are decreasing, and whether the reductions are occurring in those sectors targeted by the proposed plan. Progress towards achieving the NES will also need to be demonstrated. The suite of tools selected must be able to attribute changes in concentrations to specific sources, and to account for contributions of natural sources and secondary particulate to measured concentrations.

The most common methods used for measuring improvements over time are ambient air quality monitoring and emission inventories. Ambient monitoring of PM₁₀ and PM_{2.5} concentrations offers a direct measure of improvement, provided that monitoring is conducted over a long period. Currently, it is difficult to determine a trend because of annual variations in meteorology. Over a longer period of time, trends will be easier to establish. Alternatively, statistical methods may be employed to remove the meteorological influence from measured concentrations so that trends may be determined. However, monitoring cannot attribute changes in concentrations to specific sources and other tools are required to undertake this task.

Emission inventories, conversely, may be used to provide information on contaminant sources and, if compiled on a regular basis, can indicate relative changes over time. Inventories quantify discharges to air from different emission sources and determine the relative contributions of those sources to total emissions. Inventories are limited with regard to scope, flexibility and ability to relate sources directly to measured concentrations, and only provide a broad estimate of average emissions. The determination of source contributions to emissions only, is an important limitation as emissions discharged to air are subject to atmospheric meteorological and chemical processes that alter contaminants between point of discharge and the monitoring location. Air quality models must be used to transform emissions estimated by inventories into concentrations by simulating complicated atmospheric transport and dispersion processes. In addition, natural sources such as marine aerosol and airborne dust are difficult to determine accurately by emission inventory methods.

An alternative method exists, which incorporates positive aspects of both ambient monitoring and emission inventories, and has been widely used, internationally, by air quality managers in recent years. It is referred to as *source apportionment* and is conducted using *receptor models*. Receptor modelling of PM involves measuring concentrations of a range of chemical species at a receptor (or point of impact), applying statistical techniques to identify the main sources contributing to the measurements, and apportioning mass to those sources on a day-to-day basis (Hopke, 1991; Main and Roberts, 2001; Seinfeld and Pandis, 1998). This method can demonstrate reductions in concentrations over time, and directly attribute declining concentrations to various sources. Sources otherwise difficult to account for by emission inventories, such as marine aerosol may be quantified by this technique, and source contributions may be provided on a daily or observational basis.

Although monitoring and emission inventories are viewed as important air quality management tools for Christchurch, there are significant limitations associated with these methods. These limitations could potentially be overcome by permanently incorporating receptor modelling into the Environment Canterbury air quality management programme. Receptor models could provide alternative source attribution information to that provided by emission inventory, which would address community concerns about the quantification of source contributions and add to the “weight of evidence” required to determine and justify proposed air quality strategies. These models could also ascribe changes in concentrations to various sources, thus allowing the impact of air quality strategies contained in the proposed NRRP to be assessed, and to track progress towards achieving the NES over time. This thesis investigates the ability of a receptor model to identify the key sources, determine contributions to measured concentrations, and evaluates its potential as an effective air quality management tool for Christchurch.

Study objectives

This study recognises the potential value of receptor modelling as a source apportionment tool and for evaluating the appropriateness and effectiveness of air quality management strategies. The objectives of the study are to:

- measure fine particle concentrations in Christchurch using a filter-based method
- provide a chemical characterisation of fine particles on a seasonal basis
- investigate and trial a source apportionment method that quantifies contributions to 24-hour concentrations, rather than emissions, and takes into account natural sources and day to day variations
- characterise winter and summertime sources of fine particles and quantify their contributions to 24-hour concentrations in Christchurch
- provide a justification for including receptor modelling in air quality management programmes.

The study demonstrates how a receptor model known as Positive Matrix Factorisation (PMF) can successfully be applied to fine particle data in Christchurch. Source apportionment of PM_{2.5} is conducted and the results presented. These results may be used to verify or reject current source attribution estimates, account for natural and secondary particulate contributions when calculating emission reductions required to meet air quality targets, and to ascertain whether any additional or alternative control strategies are necessary.

Study overview

The study focuses specifically on fine particles in Christchurch as:

- $PM_{2.5}$ is the major component of PM_{10} in Christchurch on high pollution days (Foster, 1998a).
- $PM_{2.5}$ is the fraction most likely responsible for adverse health effects associated with elevated PM (Schwartz *et al.*, 1996; Schwartz and Neas, 2000; Ilabaca *et al.*, 1999; Delfino *et al.*, 1997).
- Christchurch frequently experiences elevated PM concentrations (Aberkane *et al.*, 2004a,b).

The study characterises fine particle pollution in Christchurch on a seasonal basis by identifying the major chemical constituents of $PM_{2.5}$, and their concentrations. The PMF receptor model is applied to the speciated data² to determine the key sources, and the contribution of those sources to concentrations during the summer and winter months. Issues associated with the organic and elemental carbon (OC and EC) measurements are addressed, the modelling output evaluated, and a case for including receptor modelling as an air quality management tool is presented.

The study is organised into the following twelve chapters. These are in summary:

Chapter 1: Introduces the issue addressed by the study, outlines the objectives of the research and provides a study overview.

Chapter 2: Provides background information regarding fine particles. In particular, it describes the physical properties and formation of fine particles, key chemical constituents, potential sources and briefly discusses the two key adverse impacts associated with $PM_{2.5}$.

Chapter 3: Introduces the study area and provides background with regard to meteorology, contaminant measurement, and $PM_{2.5}$ sources. It also briefly summarises management of air quality in Christchurch, including NES requirements, and measures contained in the proposed NRRP.

Chapter 4: Discusses methods of identifying and apportioning emissions and concentrations to sources, including emission inventories and receptor models. Various receptor models are described, and the basis for selecting the PMF receptor model is outlined.

Chapter 5: Reviews a selection of source apportionment studies conducted in New Zealand and overseas. The sources and chemical profiles obtained are described and used in the identification of sources resolved during this study.

² Fine particles collected on a filter may be analysed for a variety of chemical species. A matrix of concentrations of all species and observations is prepared, and is referred to as a speciated dataset.

Chapter 6: Sets out the methodology adopted by the study. The sampling location and programme, instrumentation and analytical techniques are described. The data transformation and validation techniques adopted are outlined, together with the methods of conducting the statistical analysis and the receptor modelling assessment. The methodology used to investigate the OC and EC measurements are detailed separately in Chapter 8.

Chapter 7: Is the first of several chapters presenting the results of this study. Chapter 7 describes the chemical composition of $PM_{2.5}$ in summer and winter, presents concentrations of the main chemical constituents, determines relationships between species and details the results of a preliminary source apportionment conducted using the Principal Components Analysis (PCA) and PMF receptor modelling techniques.

Chapter 8: Outlines the findings of a targeted study of OC and EC concentrations in Christchurch, conducted during the winter of 2004. Issues associated with the measurements presented in Chapter 7 are discussed, different measurement methods are compared, and the implications for the current study outlined.

Chapter 9: Presents the final source apportionment results including relative source contributions to monthly average and maximum PMF mass,³ and contributions to average and maximum summer and wintertime mass.

Chapter 10: Evaluates the source profiles by reviewing the chemical composition of each source, particle morphology (where possible), and temporal patterns in various contaminant concentrations and meteorology. This information is used to confirm whether or not the source identification makes sense on a physical basis.

Chapter 11: Assesses the quality of the model output by examining the residuals, determining the proportion of mass explained by the resolved factors and discusses potential variables contributing to unexplained mass. Revised emission inventory estimates are used as input to a box model and the results obtained are evaluated against receptor-modelled data.

Chapter 12: Provides a summary of the study findings and conclusions, and describes why receptor models should be permanently incorporated into air quality management programmes.

³ This is the sum of the source contributions and while this is essentially the same as $PM_{2.5}$ in winter, this is not necessarily the case in summer.

Chapter 2: Airborne particles

A particle may be defined as:

"A single continuous unit of solid or liquid containing many molecules held together by intermolecular forces and primarily larger than molecular dimensions ($>0.001\ \mu\text{m}$). A particle may also be considered to consist of two or more such unit structures held together by inter-particle adhesive forces such that it behaves as a single unit in suspension or upon deposit."
(Seinfeld and Pandis, 1998)

Particles suspended in a gas (airborne) may be referred to as aerosols or PM and exist in a variety of shapes and sizes. This is demonstrated in Figure 2.1 where different particle shapes are evident; from cubical, salt crystals (A) and elongated, branched hydrocarbon chains (B), to sticky agglomerations (C). The particles may be chemically uniform, or comprised of a variety of chemical compounds (Baron and Willeke, 2001). Particles are either discharged directly from a source (primary particles) or formed through chemical reactions in the atmosphere (secondary particles). Both natural and anthropogenic processes can generate particulate emissions.

This chapter provides a general introduction to airborne PM. Physical characteristics such as particle shape and size, and what these convey regarding particle origin and formation is discussed. The main chemical constituents of $\text{PM}_{2.5}$ are detailed and the formation of secondary particulate species outlined. A brief discussion of the two key adverse impacts associated with $\text{PM}_{2.5}$ is also included.

2.1 Particle shape, size and formation

2.1.1 Particle shape

Particles may be present in a variety of shapes ranging from simple spheres and rods, to more complex forms. Particle shape can be indicative of particle origin and history (Baron and Willeke, 2001). Fume particles formed from vapours discharged into the atmosphere, for example, condense into spherules, which diffuse rapidly and coagulate into branched chains. The chains increase in size, intercept one another and form large agglomerates over time. Recently formed combustion particles comprise relatively simple elongated chains, whereas aged combustion particles are denser and may be coated with organic compounds (Cachier, 1998). This is illustrated schematically in Figure 2.2, and is also demonstrated in Figure 2.1 where (B) is a fresh combustion particle and (C) constitutes an aged aerosol.

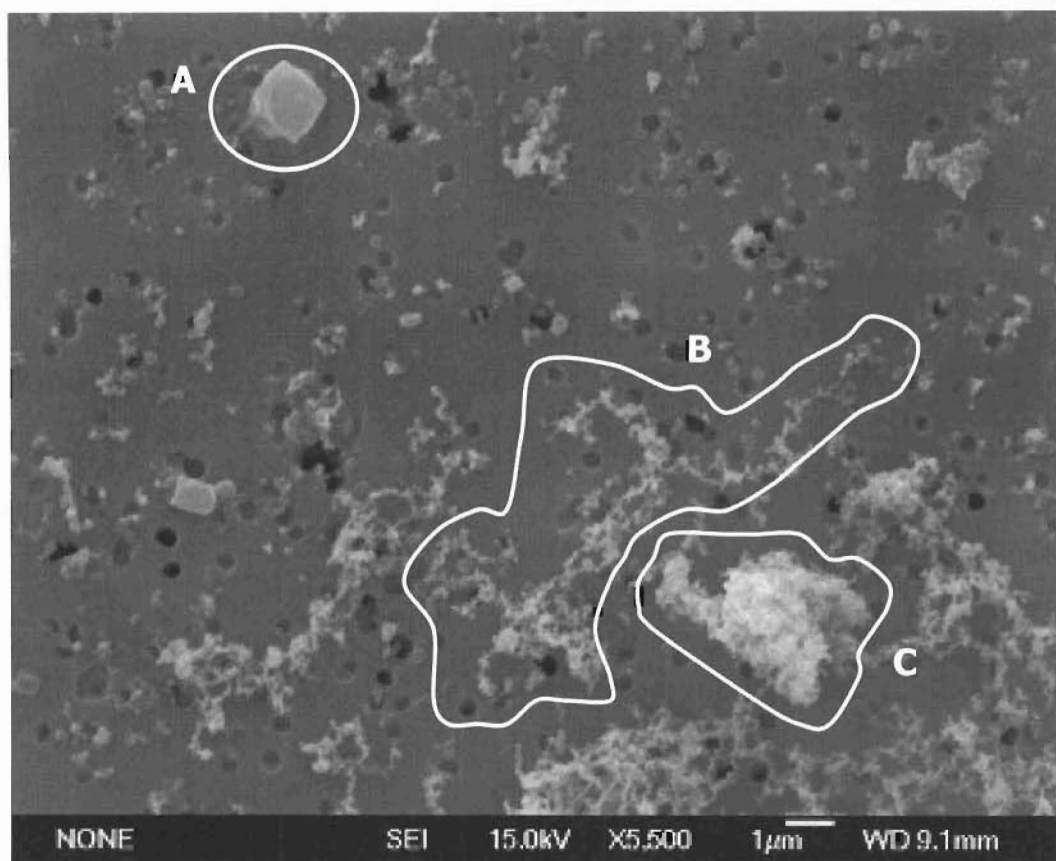


Figure 2.1 Scanning electron microscope (SEM) photograph of fine particles measured in Christchurch on a polycarbonate filter (courtesy of Perry Davy).

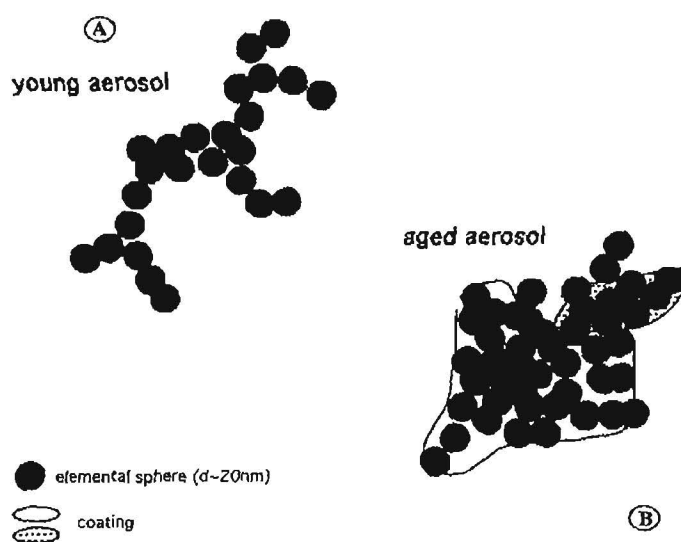


Figure 2.2 Schematic illustration of young and aged black carbon aerosols (Cachier, 1998).

The molecular structure and origin of a particle also influence its shape. As indicated, carbon compounds discharged during combustion tend to form convoluted, fractal-like structures (complex branched chains), whereas fly ash and pollens are present as distinct spheres. Chemicals such as potassium and chloride, often evident as inorganic salts, are present as crystal-like structures.

2.1.2 Particle size and formation

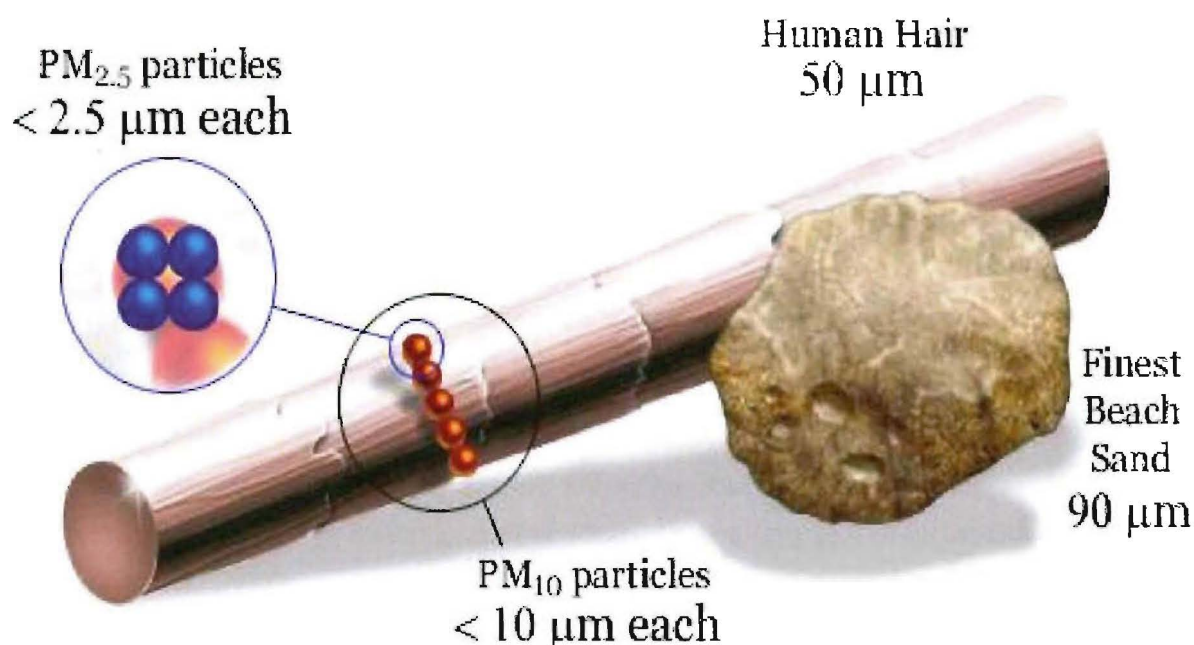


Figure 2.3 Schematic illustration of particle size in relation to human hair and beach sand (courtesy of Environment Canterbury).

Particle size (or equivalent aerodynamic diameter) is the most common characteristic of PM used for classification purposes. Aerodynamic diameter is defined by Baron and Willeke (2001) as the diameter of a standard-density sphere (1000 kg m^{-3} or 1 g cm^{-3}) with the same gravitational settling velocity as the particle being measured. Size determines particle behaviour and residence time in the atmosphere, and provides an indication of the mechanisms that created the particle (Claes *et al.*, 1998; Seinfeld and Pandis, 1998). Health effects associated with particles are directly related to particle size.

Particles are between 0.001 to 100 μm in diameter and grouped into size ranges or modes for measurement purposes. These are generally described as the fine (<2.5 μm) and coarse particle (>2.5 μm) modes (Figure 2.4).

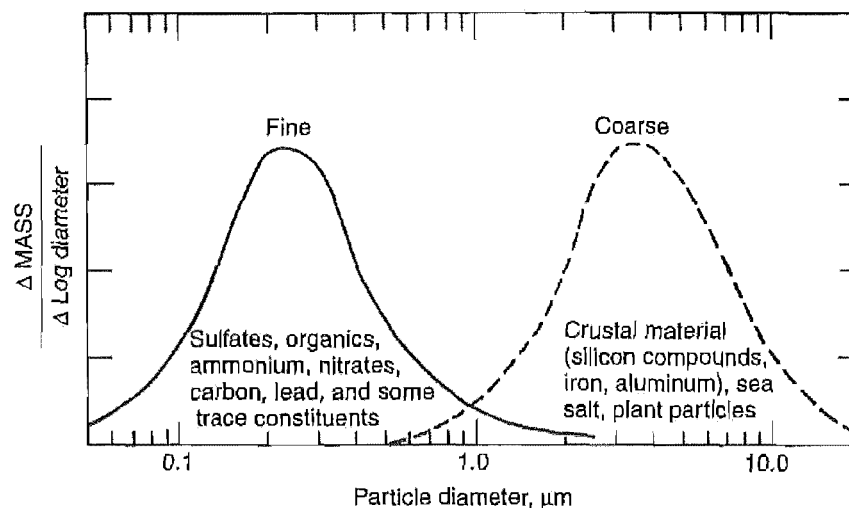


Figure 2.4 Typical urban aerosol types by particle size fraction (John, 2001).

Fine particles

Fine particles, also referred to as $PM_{2.5}$, include all particles with aerodynamic diameters of less than $2.5\ \mu m$. There are two distinct modes within the $PM_{2.5}$ size fraction. These are known as the nucleation or Aitken (up to $0.08\ \mu m$) and accumulation (between 0.08 and $2\ \mu m$) modes (Chow and Watson, 1998).

The smallest particles (nucleation or ultra-fines) are emitted directly from combustion or formed in the atmosphere through photochemical gas-to-particle conversion. The greatest numbers of particles are found in the nucleation mode but these are present in the atmosphere for limited periods of time (often less than one hour). These particles readily coagulate with existing particles or become nuclei for cloud⁴ or fog droplets (Chow and Watson, 1998; John, 2001). Individual particles are usually slightly positively or negatively charged and particles with opposite charges are attracted to each other, resulting in adhesion (coagulation). The particles are held together, or separated, by forces that depend on particle size and surface parameters (including shape, roughness and chemistry), the properties of the surrounding gas (temperature and humidity) and the mechanics of the particles (relative particle velocity and contact time; Baron and Willeke, 2001). Factors such as the amount of moisture in the air can enhance adhesion, where liquid molecules present at the point of impact increase surface tension (Baron and Willeke, 2001). The importance of photochemistry on particles in this size fraction is demonstrated by the rapid appearance and growth of nuclei mode particles at dawn (John, 2001). These particles are most numerous in close proximity to precursor emission sources in urban environments (Hobbs, 2000; Chow and Watson, 1998).

⁴ As air rises, it expands and cools below its dew point resulting in the condensation of water vapour. When the air becomes supersaturated the vapour condenses onto particles to form a small cloud of water droplets (Hobbs, 2000). These particles are referred to as cloud condensation nuclei (CCN).

Particles in the accumulation mode (approximately 0.08 to 2 μm) contain most of the fine particle mass and include finely ground dust particles, and those formed from the coagulation of nuclei mode particles and gas-to-particle conversion. Aged aerosol is likely to be present if $\text{PM}_{2.5}$ is dominated by particles in the accumulation mode (Hobbs, 2000).

Fine particles as a whole remain in the atmosphere for longer periods of time than coarse particles, and are eventually removed through dry deposition (settling) or wet deposition (rain-out) mechanisms.⁵ The length of time a particle remains suspended in the atmosphere (residence time) is a direct function of particle size and altitude. This is illustrated in Figure 2.5.

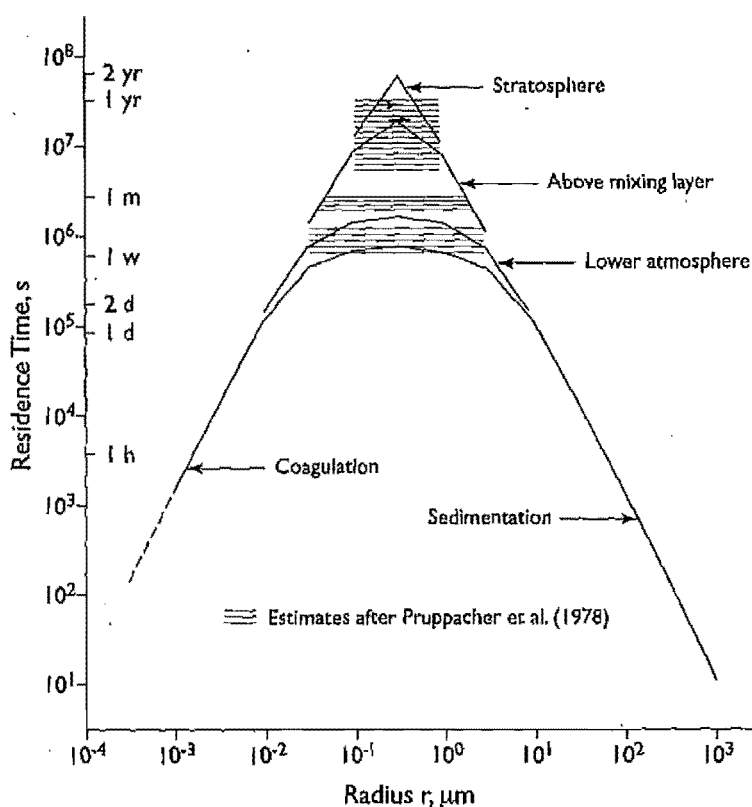


Figure 2.5 Residence time in relation to particle size and altitude (Koutrakis and Sioutas, 1996).

Combustion processes including the anthropogenic combustion of fossil fuels and biomass burning are the primary sources of particles in the $\text{PM}_{2.5}$ size fraction. Fossil fuels including solid fuel (coal and wood), liquid (diesel oil) and gas (Liquid Petroleum Gas (LPG)) are used in many cities to fuel motor vehicles and industry, and to heat residential dwellings. During combustion, fuels are oxidised at high temperatures to produce heat and combustion products including stable gaseous oxides (Brimblecombe, 1996). However, combustion is rarely complete, resulting in the emission of a mixture of gases and particles. Primary particles from combustion sources are usually less than

⁵ Wet deposition refers to the scavenging of gases and particles by clouds and precipitation, and dry deposition is direct removal through contact with vegetation, the Earth's surface and oceans, sedimentation and coagulation of aerosols (Hobbs, 2000).

0.2 μm in diameter and are subject to chemical and physical processes, leading to the formation of secondary particulate.

Coarse particles

Coarse particles ($>2.5 \mu\text{m}$) are principally produced through mechanical processes. These processes, including surface abrasion and crushing and grinding, generate coarse particles such as marine aerosol and wind-blown dust. While some marine aerosol is produced through agitation of the sea surface by the wind, the majority of the aerosol is released by gas bubbles reaching the water surface. Bursting bubbles release large and smaller droplets of water containing surface-active organic material. The large droplets fall back into the water, while the smaller ones become airborne and are transported long distances by the wind (Meszaros, 1999). Typically, 95% of marine aerosol mass comprises particles $>0.6 \mu\text{m}$ (Seinfeld and Pandis, 1998). Dust particle formation, conversely, occurs through air movement along the ground surface. Wind speeds of only 0.2 m s^{-1} are capable of ejecting soil particles into the air. These large-sized particles are generally deposited, but collision with the ground surface results in further fragmentation and re-entrainment (Brimblecombe, 1996). Bio aerosols (such as pollen, spores, leaf-litter decay and viruses) may also be found in the coarse particle mode, with some, such as viruses and bacteria, present in the fine particle fraction ($<2.5 \mu\text{m}$). Coarse particles do not remain in the atmosphere for long periods as high sedimentation rates lead to quick removal (Seinfeld and Pandis, 1998).

From a health perspective, fine particles are of greater concern than coarse particles. Fine particles are predominantly derived from anthropogenic combustion sources and have the ability to travel further into the human lung. In addition, potentially toxic chemicals, such as acids, heavy metals and polycyclic aromatic hydrocarbons (PAHs) are predominantly found in the fine particle fraction (Brook *et al.*, 1997).

2.2 Chemical composition and potential sources

Airborne particles are comprised of numerous chemical compounds and may be produced by anthropogenic and natural sources. The chemical constituents of fine particles include carbon compounds, water-soluble inorganic salts, and metallic elements. These chemical species can provide an initial indication of particle origin.

2.2.1 Elemental and organic carbon (EC, OC)

Elemental/black carbon (EC/BC) is discharged directly into the atmosphere during fossil fuel combustion. Fuels are oxidised and pyrolysed⁶ by high temperature combustion processes into molecules, which are released into the atmosphere. Nuclei form and rapidly develop into larger compounds through particle surface reactions. These particles form chain-like aggregates resulting in

⁶ Oxidation refers to a process where oxygen is combined with another substance or where an electron is removed from an element or compound, whereas pyrolysis refers to the chemical decomposition of a substance by the action of heat.

visible particles up to several microns in size, chemically similar to impure graphite. Other carbon compounds included in this category are high molecular weight, non-volatile organic species (Chow and Watson, 1998).

Table 2.1 Characteristics of OC and EC and source origin (adapted from Main and Roberts, 2001).

Species	Primary/ secondary	Major anthropogenic sources	Comments
Organic carbon	P/S	Domestic wood combustion, vegetative burning, motor vehicles and cooking	Carbon compounds with more than 20 atoms. Species often transfer between the gas and particle phases.
Elemental carbon	P	Domestic wood combustion, motor vehicles and cooking	Similar to impure graphite and forms into chain-like aggregates.

EC can be produced by a variety of sources including residential heating, industry and diesel vehicles. Identifying sources contributing to emissions of this substance is difficult, due to its non-uniqueness. The proportion of OC to EC in emissions is considered indicative of source origin and is often used in this capacity. Measures of OC and EC, however, are fully dependent on the measurement and analytical methods used, further complicating the source identification process. Table 2.2 presents estimated fuel-specific carbon emission rates based on those outlined in Seinfeld and Pandis (1998). They illustrate the types of ratios used to differentiate between carbon emitting sources. Ratios vary depending on combustion technology and fuel composition, and should not be used independently of other verifiable information to identify sources. This is discussed further in Chapter 8.

Table 2.2 Source-based OC and EC emission rates (g kg^{-1}) and ratios (adapted from Seinfeld and Pandis, 1998).

Source	Organic carbon	Elemental carbon	OC/EC ratio - based on maximum values
Fireplace			
Hardwood	4.7	0.4	12:1
Softwood	2.8	1.3	2:1
Motor Vehicles			
Nuncatalytic	0.04-0.24	0.01-0.13	2:1
Catalytic	0.01-0.03	0.01-0.03	1:1
Diesel	0.7-1.0	2.1-3.4	1:3
Furnace (natural gas)			
Normal	0.0004	0.002	1:5
Rich	0.007	0.12	1:17

OC compounds are defined by Chow and Watson (1998) as those with more than 20 carbon atoms. These particles may be discharged directly into the atmosphere or formed by the condensation of organic gases. Hydroxyl (OH) and nitrate (NO_3) radicals oxidise these gases and the oxidation products accumulate. The low-volatile products of these reactions condense on the available particles to achieve equilibrium between the gas and particle phase (Seinfeld and Pandis, 1998). However, accurate measurement of these substances is problematic, due to the tendency for organics to

continuously transfer between the gas and particle phase (which is temperature dependent). The measurements obtained usually represent carbon atoms only and factors must be applied to the data, based on literature values, to account for the other chemical species present. For example, OC measurements may be multiplied by values ranging from 1.2 to 1.6 to account for the oxygen, nitrogen and hydrogen constituents found in organic compounds (Seinfeld and Pandis, 1998). Selection of a robust multiplier is dependent on local knowledge of the species present and the level of gas-to-particle partitioning.

A large number of organic compounds are present in urban air. These include *n*-alkanes, *n*-alkanoic acids, *n*-alkanals, aliphatic dicarboxylic acids, diterpenoid acids and retene, aromatic polycarboxylic acids, PAHs, polycyclic aromatic ketones and quinones, steroids, N-containing compounds, regular steranes, pentacyclic triterpanes, and iso- and anteiso-alkanes (Seinfeld and Pandis, 1998). Some of these species are known carcinogens and associated with significant health effects. Of particular concern are the PAHs. These are formed during the incomplete combustion of organic matter and consist of two or more fused benzene rings. The United States Environmental Protection Agency (USEPA) has identified 16 key PAH species with benzo(a)pyrene used as the indicator species of carcinogenicity (Gunatilaka, 2001).

OC is derived from the same sources as EC, that is, residential heating, industry and motor vehicles. The relative proportion of these two species in emissions can indicate particle origin. OC is more abundant than EC in emissions from low temperature combustion processes such as biomass burning. However, as indicated in Table 2.2, the burning of softwood produces a similar OC/EC ratio as that discharged from non-catalytic motor vehicles. This suggests that in areas where wood combustion is dominated by the burning of pine, the ratio approach may not be useful. Nevertheless, there are several unique organic species that may be used as markers for particular sources. For example, dehydroabietic acid, pimaric acid, isopimaric acid, retene and sandaracopimaric acid are used as indicators of wood smoke, and steranes and pentacyclic triterpanes are indicative of motor vehicle emissions (Seinfeld and Pandis, 1998).

2.2.2 Inorganic ions (NO_3^- , SO_4^{2-} , NH_4^+)

Inorganic ions⁷ including nitrates, sulphates and ammonium are all secondary particulate species formed by chemical reactions in the atmosphere. The OH and NO_3 radicals have an important role in the formation of these species and it is useful therefore to understand how these radicals are derived. OH radicals are formed when ozone (O_3) is decomposed by solar UV radiation into oxygen and charged oxygen atoms (O^*). The OH radical, a highly reactive oxidant, immediately reacts with several contaminants including carbon monoxide (CO) to form carbon dioxide (CO_2), nitrogen dioxide (NO_2) to form nitric acid (HNO_3), hydrogen sulphide (H_2S) to form sulphur dioxide (SO_2), SO_2 to form

⁷ An ion is an electrically charged atom.

sulphuric acid (H_2SO_4), and formaldehyde to form CO (Hobbs, 2000). The concentration of the OH radical is lower during the nighttime period and greatest during the day. As such, reactions with the OH radical predominantly occur during daylight hours.

Table 2.3 Characteristics of major inorganic ions present in $\text{PM}_{2.5}$ and source origin (adapted from Main and Roberts, 2001).

Species	Primary/ secondary	Major anthropogenic sources	Comments
Nitrate (NO_3^-)	S	NO_x from fossil fuel combustion (energy, mobile sources, biogenics, and industrial processes).	Ammonium nitrate is a principal component of secondary aerosol in locations such as western USA. Natural sources: soil, forest fires, lightning.
Sulphate (SO_4^{2-})	S	SO_x from fossil fuel combustion (energy generation, industrial processes, mobile sources).	Ammonium sulphate is the primary component of $\text{PM}_{2.5}$ in the eastern US. Natural sources: sea spray sulphate, volcano gaseous sulphur, forest fires.
Ammonium (NH_4^+)	S	Ammonia from animal husbandry, fertilizer use, sewage. Also mobile sources, combustion, industrial processes.	Important compound in nitrate and sulphate chemistry. Natural sources: undisturbed soil, wild animals.

At night, the nitrate radical (NO_3) becomes the most important oxidising agent and reacts with a number of other atmospheric species. NO_3 is formed when NO_2 and O_3 are present in the same air mass (Seinfeld and Pandis, 1998).



NO_2 and the NO_3 radical exist in equilibrium with N_2O_5 . NO_3 is less reactive than OH, but is present in higher concentrations. During the day, NO_3 is photolysed by solar radiation, and also reacts with NO (Hobbs, 2000; Seinfeld and Pandis, 1998).



Sulphate (SO_4^{2-})

Sulphates are water-soluble inorganic ions that usually exist in the fine particle fraction. These chemical species are particularly effective at scattering light and can significantly impair visibility (see Section 2.3.2).

Sulphate is formed through the oxidation of sulphur gases by the OH radical to SO_2 , which is further oxidised to sulphate. This is summarised by Claes *et al.* (1998) as follows:



The precursors of sulphates (sulphur gases) are generated by natural and anthropogenic processes. In marine environments, phytoplankton produce sulphur gases in the form of dimethyl sulphide (DMS), which may be oxidised to SO_2 (Meszaros, 1999; Hobbs, 2000; Claes *et al.*, 1998). On land, SO_2 is discharged directly by anthropogenic combustion processes. Approximately 65% of SO_2 is subject to further oxidation by the OH radical forming sulphur trioxide (SO_3) and H_2SO_4 (Hobbs, 2000). The acid reacts with gaseous ammonia (NH_3) and produces the main atmospheric forms of sulphate, ammonium sulphate ($(NH_4)_2SO_4$) and ammonium bisulphate (NH_4HSO_4). Additional sulphate species, such as sodium sulphate (Na_2SO_4), may be found in coastal areas where H_2SO_4 is neutralised by the sodium chloride (NaCl) compounds found in marine aerosol (Equation 9; Chow and Watson, 1998). Sulphate production in these areas may increase when low tides coincide with daylight hours. Sulphur producing algae are exposed to sunlight at this time, thus increasing sulphate production (Renoux *et al.*, 1981 as cited in Meszaros, 1999). Reactions between H_2SO_4 vapour and marine aerosol can lead to an apparent "chloride deficit" in aerosol identified as of marine origin (Seinfeld and Pandis, 1998):



Nitrate (NO_3^-)

Nitrate is also an important secondary particulate species and is formed by the oxidation of NO_2 to HNO_3 , which then reacts with NH_3 to form ammonium nitrate (NH_4NO_3), or with NaCl to form sodium nitrate ($NaNO_3$). Nitric oxide (NO) is discharged by a variety of processes including microbiological activity in soils, lightning strikes, and anthropogenic sources such as fossil fuel combustion, motor vehicles and residential heaters. NO molecules are oxidised to NO_2 and HNO_3 .

During the day, NO_2 is oxidised by the OH radical to produce HNO_3 .

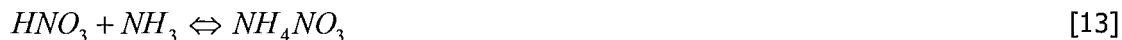


During the night, NO_3 (formed via Equation 1) is converted to HNO_3 via two mechanisms:



In the presence of NH_3 , HNO_3 forms NH_4NO_3 . These reactions occur at low temperatures (often at night) and decomposition takes place during daylight hours (Meszaros, 1999). The reaction between NH_3 , HNO_3 , and NO_3^- is a reversible gas/particle equilibrium, which changes in response to varying

temperatures and humidity. Additional species, such as NaNO_3 , may be found in coastal environments where HNO_3 reacts irreversibly with marine aerosol (Chow and Watson, 1998).



Ammonium (NH_4^+)

Particulate ammonium is usually present as $(\text{NH}_4)_2\text{SO}_4$, NH_4HSO_4 and NH_4NO_3 . As indicated previously, these compounds are formed in the atmosphere by reactions with NH_3 , oxides of nitrogen (NO_x) and SO_2 gases. NH_3 is released from animal urine and microbiological activity in soils (Hobbs, 2000; Brimblecombe, 1996).

The neutralisation of H_2SO_4 by NH_3 occurs as follows:



The formation of NH_4NO_3 is described in Equation 13.

2.2.3 Major elements

The elemental species measured in ambient air are dependent on location and the types of activity present in an area. Table 2.4 outlines common chemical species found in coastal, urban environments such as Christchurch. These include a combination of species associated with marine aerosol (such as sodium and chlorine), wood combustion (potassium), coal combustion (selenium), soil (aluminium, silicon and iron), industry (iron and sulphur), and motor vehicles (titanium, sodium and chromium).

Trace elements, if present in relatively low concentrations, are not usually of concern. However, elements may accumulate in plants and plant-eating animals and have ecological consequences. Accumulation of heavy elements such as cadmium, lead, arsenic, mercury and selenium can be an issue in some areas.

Table 2.4 **Characteristics of major elemental species present in PM_{2.5} and source origin (adapted from Main and Roberts, 2001).**

Species	Primary/ secondary	Major anthropogenic sources	Comments
Na	P	Sea water, open playas, de-icing	
Cl ⁻	P	Sea water	Also vegetative burning
K	P	Vegetative burning	Prescribed burns, forest fires, residual wood combustion, meat charbroiling
Ni	P	Residual oil combustion	
Ca	P	Crustal material	Also smelters, incinerators
Fe	P	Crustal material	Also smelters, incinerators, steel blast furnace
V	P	Residual oil combustion	
Al	P	Crustal material	
Si	P	Crustal material	Also coal-fired boiler
S	P/S	Residual oil combustion	Also smelters, antimony roaster
P	P	Fuel combustion	Not generally present in vegetative burning emissions
Pb	P	Vehicle exhaust	Lead is generally undetectable in vehicle emissions at present due to the introduction and use of unleaded fuel
Br	P	Vehicle exhaust	
Mn	P	Steel blast furnace, ferro manganese	
Cl	P	Incinerator, marine	
Cu	P	Smelter	
Ti	P	Crustal material	

2.3 Impacts of fine particles

Fine particles, present in indoor and outdoor ambient air adversely affect both human and animal health, cause vegetation damage, soil and corrode buildings, and degrade visibility. In Christchurch, the potential for substantial human health and amenity effects is considerable due to the prevalence of high PM_{2.5} concentrations in the city. The following discussion will focus on human health and amenity impacts.

2.3.1 Health effects

The impact of particulate pollution on human health has been an issue for many years. Although investigations in the past have focused on total suspended particulate (TSP) and PM_{10} , in more recent times the potential effects of the $PM_{2.5}$ fraction on health has become of greater concern.

Particle properties, such as size, shape, density and reactivity, determine how particles are transported, react in the human respiratory tract and impact on health. PM_{10} is generally exhaled but smaller, inhalable particles (such as $PM_{2.5}$) penetrate deeply into the lung. Individuals most at risk include those with chronic lung disease, asthmatics, infants and the elderly. Health effects range from minor irritation of the eyes and nose, to exacerbation of existing respiratory and cardiac illnesses among young children and the elderly. Health studies conducted in Christchurch confirm that effects documented overseas also occur in New Zealand. It is estimated that for every $10 \mu g m^{-3}$ increase of PM_{10} , a 1% increase in "all-cause" mortality⁸ and a 4% increase in respiratory mortality occurs (Hales *et al.*, 1999). Based on these studies, it has been estimated that 40-70 deaths per year may be associated with PM_{10} concentrations in Christchurch (Wilton, 1999). Until recently, study of the impacts of air pollution on health in New Zealand has been limited. A major study, jointly funded by the MfE, Ministry of Transport (MoT) and the Health Research Council, is currently underway and is programmed to run for three years. The study will address the causes and costs associated with PM-related health effects and will provide a suite of management options that may be used to reduce these impacts. The study is due for completion early in 2006.

A number of international studies have focused on the health effects associated with the $PM_{2.5}$ size fraction. It has been suggested that $PM_{2.5}$ may be responsible for the adverse health effects associated with PM. Greater associations were found between $PM_{2.5}$ and specific health effects than for coarse particles ($PM_{10-2.5}$), as the smaller size of the particles increases the capacity for respiratory penetration and retention (Schwartz *et al.*, 1996; Schwartz and Neas, 2000; Ilabaca *et al.*, 1999; Delfino *et al.*, 1997). However, not all studies agree with these findings and further work in this area is required. Despite these differences, there is a general consensus that fine particles travel further into the lung and are likely to have greater impacts than PM_{10} .

Although many studies have reported links between PM and human health, there remain some unresolved issues. These are outlined briefly below:

- An extensive review of epidemiological studies undertaken in the United States (US) and in Europe, was conducted by Vedal (1997). He found that the statistical associations between PM and health were not always consistent or strong.

⁸ All cause mortality refers to all deaths recorded for a particular population.

- Evidence demonstrating the body's biological response to PM and how this impairs human health has yet to be presented.
- There are poor correlations between outdoor and indoor pollutant concentrations (Sexton *et al.*, 1984; Morandi *et al.*, 1988; Lioy *et al.*, 1990; Pellizzari *et al.*, 1993; Suh *et al.*, 1993 as cited in Chow and Watson, 1998).

Although these are important issues, a precautionary approach to air quality management is necessary to ensure that community health is adequately protected. It may take many years for sufficient toxicological evidence to be collected and this delay should not prevent immediate action to protect community health. The statistical associations between PM and health are strong enough to warrant preventative action. PM_{2.5} is the particulate fraction, and ambient concentrations probably lower than, those most people are exposed to (Chow and Watson, 1998). Therefore, strategies are required to address ambient PM_{2.5} concentrations.

2.3.2 Amenity effects

Fine particles viewed at a distance can degrade visibility and reduce amenity, even at low concentrations. Visual impacts occur as a consequence of visibility reduction or degradation, which is defined by the USEPA (1999) as:

Visibility: *The ability to see an object or scene as affected by distance and atmospheric conditions; to perceive form, colour and texture.*

Visibility Reduction: *The impairment or degradation of atmospheric clarity. It becomes significant when the colour and contrast values of a scene to the horizon are altered or distorted by airborne impurities.*

The ability of an observer to view an object is determined by the optical properties of the atmosphere, the amount and distribution of available light, characteristics of the object being viewed and properties of the human eye (Seinfeld and Pandis, 1998). Visibility is reduced when light is scattered and absorbed by fine particles and gases to form haze.

Visibility reduction is considered to be a significant issue in areas such as the United States (US) where legislation has been introduced to protect visibility in areas of great scenic importance (such as national parks and wilderness areas). A review of amenity issues in New Zealand found that degraded visibility, in the form of brown or white haze, was evident over cities such as Christchurch and Auckland (Environet Ltd, 2003). Accordingly, it was suggested that it may be appropriate for a national visibility or guideline standard to be introduced eventually.

A study of visibility was conducted in Christchurch during 2000/2001 to investigate the causes of haze in the city. This haze was evident in the winter months, and frequently obscured views to the Port Hills and Southern Alps. Fine particles were the greatest contributor to reduced visibility, and visibility was worse on days when $PM_{2.5}$ was elevated (Wilton, 2003). Haze was also present on days when $PM_{2.5}$ concentrations were low, and did not pose a significant health risk. This suggests that amenity in Christchurch may be reduced at very low concentrations. The study concluded that motor vehicles and secondary particles were the most significant contributors to morning haze.

The Christchurch visibility study raised some important issues that may need to be addressed in future years. Management measures designed to reduce emissions from residential heating are unlikely to reduce morning haze. The community may perceive this as indicative that measures proposed in the NRRP are inappropriate and ineffective at addressing the air quality issue in Christchurch. Good knowledge of the sources contributing to $PM_{2.5}$ and visibility reduction is essential, and the investigation of more effective source apportionment methods will allow better identification of those sources contributing to visibility reduction.

2.4 Summary

Particles exist in many different shapes and sizes, which can provide an indication of source origin and formative mechanisms. The most common characteristic used to classify particles is equivalent aerodynamic diameter or size. Particles are usually grouped in the fine ($<2.5 \mu m$) or coarse ($>2.5 \mu m$) modes. Fine particles are generally of combustion origin and include both primary and secondary (formed through chemical reactions in the atmosphere) particles. Coarse particles are produced by mechanical processes and only remain in the atmosphere for short periods of time. Chemicals commonly present in PM include OC and EC, nitrate, sulphate, ammonium, potassium, sodium, chlorine, iron, aluminium, silicon and sulphur. The fine particle fraction is of greatest concern owing to extended retention time in the atmosphere, capacity to travel further into the human lung (resulting in adverse health effects), and ability to scatter light contributing to visibility degradation. Management of fine particles is necessary to protect community health, and an understanding of the sources contributing to concentrations is mandatory.

Chapter 3: Air quality in Christchurch and its management

Air quality has been a major issue in Christchurch for many years. Factors such as topography, meteorology, and number and type of emission sources combine to create an unhealthy wintertime living environment for the young, old and those with pre-existing pulmonary or respiratory health problems. Concerns regarding health impacts associated with elevated particulate levels in Christchurch have led to substantial study of degraded air quality and its causes. Stringent, but necessary, air quality measures targeting major emission sources, have subsequently been introduced. This chapter places the study in context by briefly describing the study area, its meteorological characteristics, air quality, contaminant sources and management over time.

3.1 Study area

Christchurch is situated on the eastern coastline of the South Island of New Zealand and has a residential population of approximately 344,000. The metropolitan area extends from the Port Hills in the south to the gently sloping Canterbury Plains in the north (Figure 3.1). These topographical features, combined with the Southern Alps to the west and the coastline to the east, have significant impacts on local wind patterns and meteorology. Temperature inversions occur frequently during the wintertime, trapping emissions at the surface, resulting in elevated contaminant concentrations.

3.2 Meteorology

The magnitude and frequency of wintertime fine particle events in Christchurch is largely driven by meteorological factors. There are three key meteorological phenomena that influence contaminant dispersion in Christchurch; temperature inversions, complex local wind patterns and the “blocking effect” associated with the Southern Alps (Kossmann and Sturman, 2004; Sturman *et al.*, 2003; Sturman and Tapper, 1996).

During winter, anticyclonic synoptic weather conditions over Christchurch often result in cold, calm and clear periods, particularly overnight (Kossmann and Sturman, 2004). Radiative cooling of the land surface after sunset can result in the formation of nocturnal temperature inversions. Inversions exist when the air temperature increases, rather than decreases, with rising altitude. These inversions form a layer where vertical turbulence is restricted and atmospheric mixing is inhibited. The inversion layer itself may be greater than 100 m deep but the mixing height or depth restricted to a sub-layer of only 30 m (Gimson, 1998). Figure 3.2 illustrates the formation and impact of wintertime temperature inversions on air quality in Christchurch. The conditions that lead to the development of temperature inversions are often the same as those that require householders to heat their dwellings. Householders returning from work often light their fires around 5 pm coinciding with the onset of the

radiation temperature inversion. At this time, particulate emissions are at their greatest and there is the least capacity for their dispersion. Emissions accumulate and elevated particulate concentrations occur. Emissions discharged at this time of day have a greater impact on 24-hour concentrations than daytime emissions (Wilton, 2001b). During the day radiative heating of the land surface by the sun results in the erosion of the temperature inversion, and increased wind speeds readily disperse any contaminants present (Kossmann and Sturman, 2004).



Figure 3.1 Christchurch and its surroundings.

Geographical features such as the Port Hills, Canterbury Plains and the coastline are conducive to the formation of complex wind patterns in Christchurch (McKendry *et al.* 1986,1987; Sturman *et al.*, 2003). During the night, cool air at the surface, denser than warmer air aloft, drains down slope towards the coast. These air flows, known as cold air drainage or katabatic flows, originate from the Port Hills or from the gentle slopes of the Canterbury Plains. The flows are variable and may or may not reach the central Christchurch area. Contaminants originating in one part of Christchurch are mixed with emissions generated elsewhere, and transported throughout the Christchurch airshed. Concentrations of $PM_{2.5}$ measured at St Albans, for example, comprise both locally generated contaminants and those from other parts of Christchurch (and beyond). Daytime wind speeds are more elevated, than those evident overnight, and predominantly from a northeasterly direction. Ventilation is improved and pollutants are rapidly dispersed.

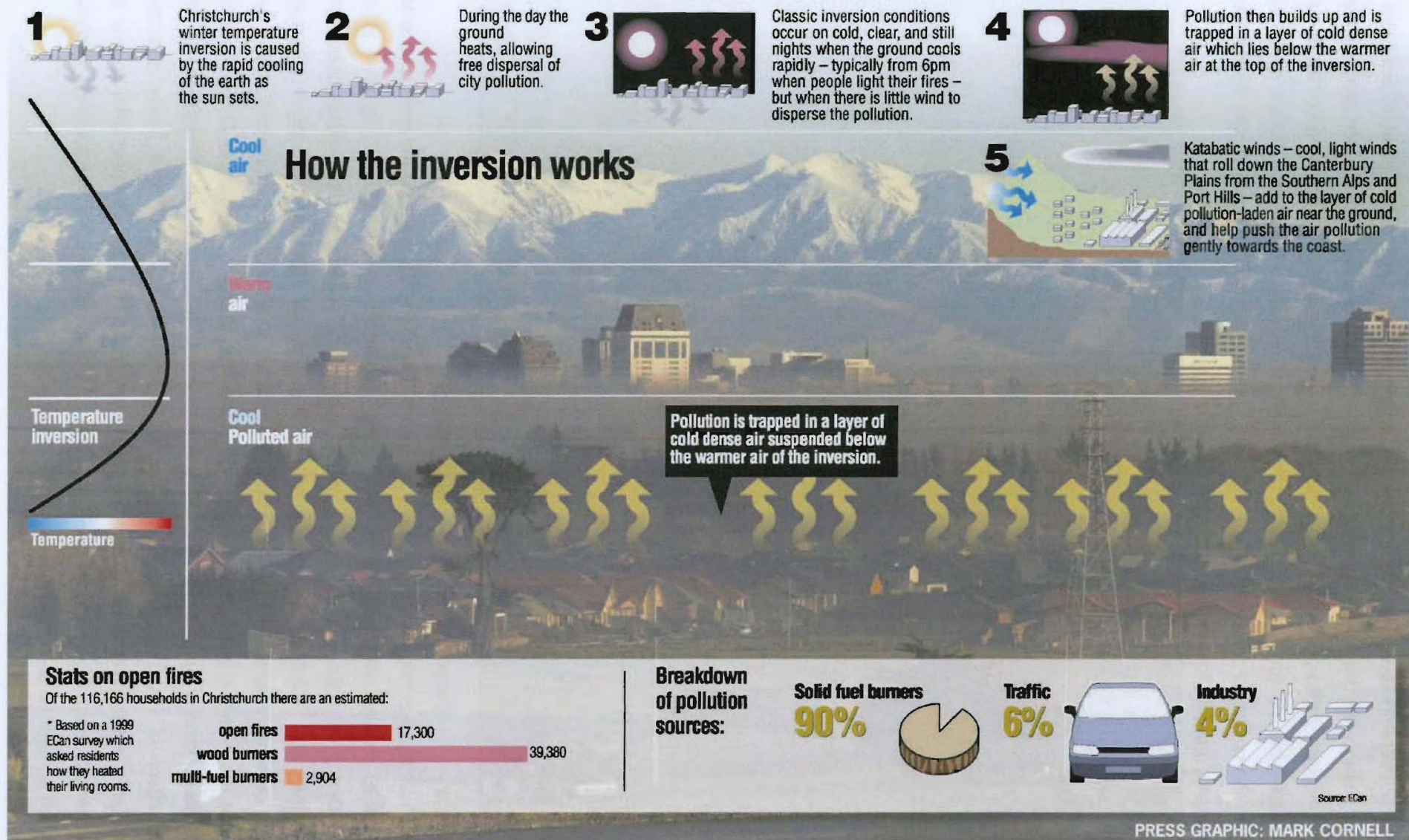


Figure 3.2 Development of a temperature inversion in Christchurch (as depicted in *The Christchurch Press*).

In summary, conditions conducive to the development of temperature inversions are often the same as those that lead to householders heating their dwellings. Inversions trap emissions and the local winds transport pollutants across the city. The contaminants accumulate and elevated concentrations occur. Although meteorology cannot be controlled, it is possible to reduce overall emission loadings so that under worst-case meteorological conditions, exceedences of air quality guidelines and standards do not occur.

3.3 Air quality measurement

Air quality monitoring in Christchurch was initiated by the Department of Health in the 1960s. Monitoring was conducted fairly sporadically until 1988 when a permanent, continuous monitoring site was established at Packe Street in St Albans. Ten years later, redevelopment of the site culminated in the establishment of a new Christchurch residential monitoring site at Coles Place, St Albans. Environment Canterbury managed the new site from its inception in 1998. Subsequently, monitoring has been conducted in numerous locations around Christchurch, and in other regional centres. Comprehensive assessments of air quality measurements obtained from these areas are provided in Environment Canterbury's annual air quality monitoring reports (e.g. Aberkane *et al.*, 2004a,b).

3.3.1 Routine contaminant monitoring at Coles Place, St Albans

Air quality measurements collected at St Albans, Christchurch, are used to establish long-term trends in air quality. Contaminants measured routinely at the permanent residential monitoring site at Coles Place include PM₁₀, PM_{2.5}, CO, SO₂ and NO_x. These measurements are evaluated against ambient air quality guidelines and standards (NES), as established by the MfE (MfE, 2002,2004), to assess whether air quality is an issue in Christchurch. Key guidelines and NES values are outlined in Table 3.1. The NES allows for a number of exceedences of each threshold concentration annually. For example, one annual exceedence of the 24-hour average threshold concentration of 50 µg m⁻³ for PM₁₀ is permitted.

A guideline for PM_{2.5} has not yet been established by the MfE. It was originally intended that a guideline would be introduced by 2004, after conducting an investigation of PM_{2.5} in New Zealand. However, this process has been superseded by development of the national standards. Nevertheless, it has been recommended that PM_{2.5} data be assessed against a 24-hour average monitoring value of 25 µg m⁻³ (MfE, 2002).

In addition to setting guidelines and standards, the MfE grouped ambient concentrations into a series of management action categories. Ambient concentrations greater than 66% of the guideline were classified as being in the "alert" category (e.g. for 24-hour average PM₁₀ this refers to concentrations between 33 and 50 µg m⁻³), and those exceeding the guideline were in the "action" category. These categories are outlined in Table 3.2.

Table 3.1 Ambient air quality guidelines and National Environmental Standards (MfE, 2002; 2004).

Contaminant	Status	Concentration	Averaging period	Permitted exceedences
CO	Guideline NES	30 mg m ⁻³	1-hour	N/A
		10 mg m ⁻³	8-hour	1 annually
PM ₁₀	NES	50 µg m ⁻³	24-hour	1 annually
	Guideline	20 µg m ⁻³	Annual	N/A
NO ₂	NES	200 µg m ⁻³	1-hour	9 hours annually
	Guideline	100 µg m ⁻³	24-hour	N/A
SO ₂	NES	350 µg m ⁻³	1-hour	9 hours annually
	NES	570 µg m ⁻³	1-hour	0
	Guideline	120 µg m ⁻³	24-hour	N/A

Table 3.2 MfE management action categories (MfE, 2002).

Category	Measured value	Comment
Action	Exceeds the guideline value	Exceedences of the guideline are a cause for concern and warrant action if they occur on a regular basis.
Alert	Between 66% and 100% of the guideline value	This is a warning level, which can lead to exceedences if trends are not curbed.
Acceptable	Between 33% and 66% of the guideline value	This is a broad category, where maximum values might be of concern in some sensitive locations, but are generally at a level that does not warrant dramatic action.
Good	Between 10% and 33% of the guideline value	Peak measurements in this range are unlikely to affect air quality.
Excellent	Less than 10% of the guideline value	Of little concern: if maximum values are less than a 10 th of the guideline, average values are likely to be much less.

Figure 3.3 to Figure 3.6 group contaminant concentrations measured at St Albans from 1995 to 2002 into the MfE management action categories (provided by Teresa Aberkane, Environment Canterbury). The proportion of concentrations within a particular category, for a given year and contaminant, is presented. The PM₁₀ concentrations are based on measurements collected by a Tapered Element Oscillating Microbalance (TEOM) analyser operating at 40°C. Environment Canterbury has replaced this instrument and will be converting the PM₁₀ data into concentrations equivalent to those provided by the new technology, to allow inter-annual comparisons (see Environment Canterbury's website). The data presented therefore are subject to change.

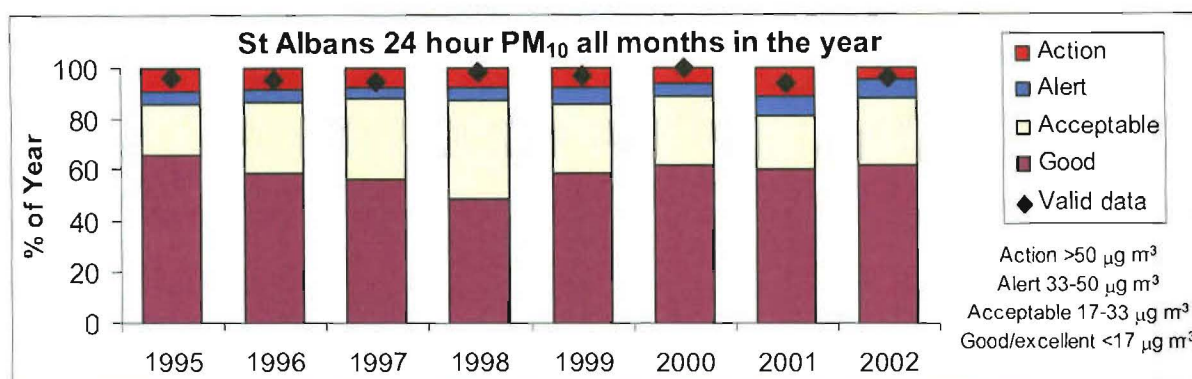


Figure 3.3 Comparison of 24-hour average PM₁₀ concentrations at St Albans with MfE management categories. 'Valid data' indicates the proportion of the year for which valid data were available. Source: Environment Canterbury.

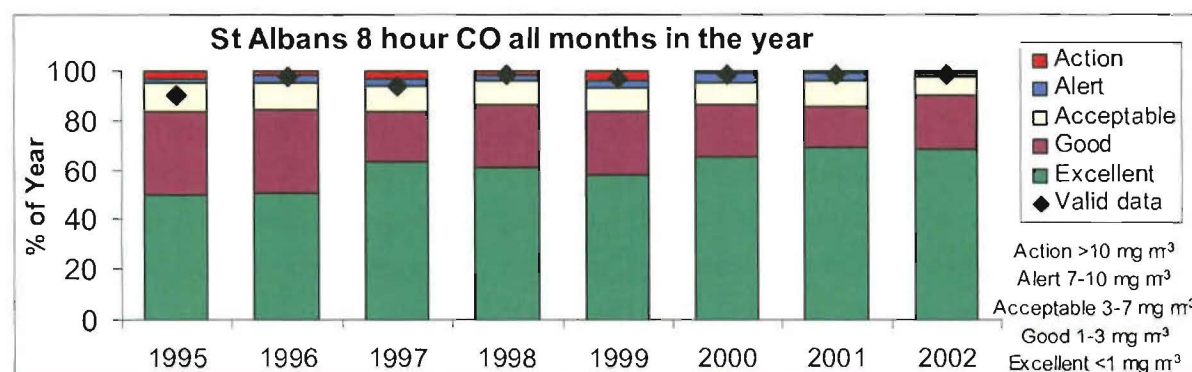


Figure 3.4 Comparison of 8-hour average CO concentrations at St Albans with MfE management categories. 'Valid data' indicates the proportion of the year for which valid data were available. Source: Environment Canterbury.

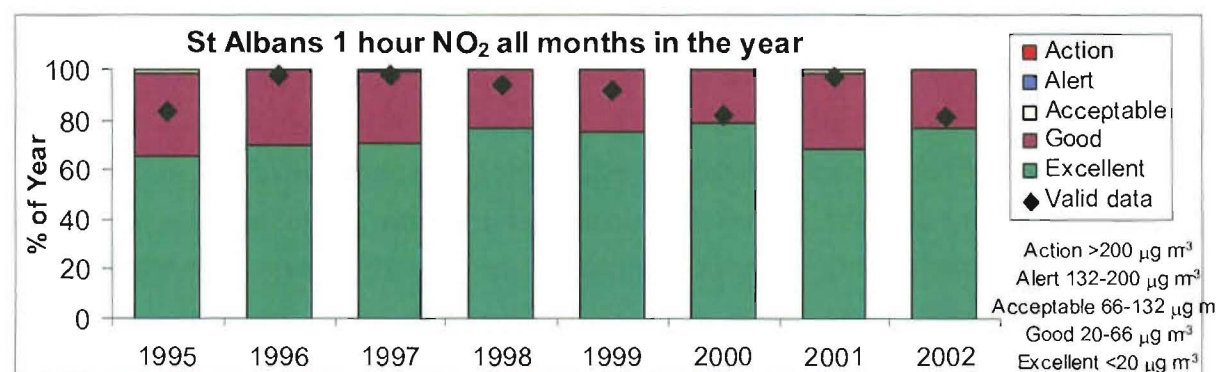


Figure 3.5 Comparison of 1-hour average NO₂ concentrations at St Albans with MfE management categories. 'Valid data' indicates the proportion of the year for which valid data were available. Source: Environment Canterbury.

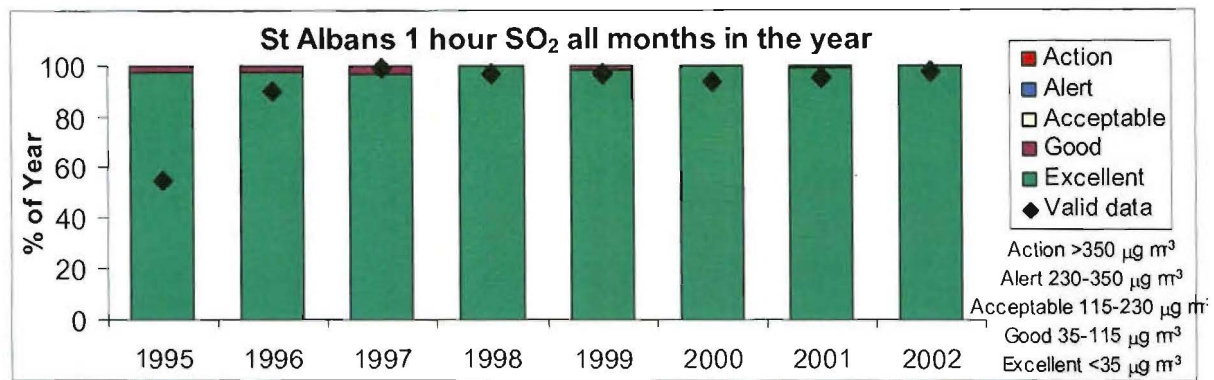


Figure 3.6 Comparison of 1-hour average SO₂ concentrations at St Albans with MfE management categories. 'Valid data' indicates the proportion of the year for which valid data were available. Source: Environment Canterbury.

The annual proportion of PM₁₀ exceedences (action category) varies from year to year. The greatest number of exceedences occurred in 2001 with 11% of daily PM₁₀ exceeding the NES. This is higher than that indicated for most years where the proportion of exceedences was around 8 to 9%. There are no concentrations that fall within the excellent category and no clear improvement evident. CO also exceeds guidelines, albeit infrequently, with exceedences occurring between 1995 and 1999. The majority of concentrations were in the excellent category, which appears to have increased over time, suggesting that some improvement has occurred. Concentrations of NO₂ and SO₂ were predominantly in the excellent and good categories, and there were no exceedences of the NES from 1995 to 2002. It appears that NO₂ concentrations may have also improved over time with a slight increase in the proportion of concentrations in the excellent category. Almost all SO₂ is within this category.

On the basis of these data, it is difficult to indicate the degree to which air quality has or has not improved between 1995 and 2002. It appears that concentrations of CO and NO₂ may have improved over time with very little change evident in PM₁₀ and SO₂. However, meteorology has a significant impact on measured concentrations, confounding trend determination. Environment Canterbury recently commissioned consultants to conduct a trend analysis of PM₁₀ in Christchurch. PM₁₀ concentrations from 1996 to 2003 were normalised to remove meteorological influences from the data, and a reduction in the order of 2 to 6% per year was found (Marsh and Wilkins, 2004). Similar analyses could potentially be conducted to determine trends for other contaminants. Nevertheless, it is clear that PM₁₀ is the contaminant of greatest concern in Christchurch, with the highest proportion of concentrations in the alert and action categories. Although some exceedences of the 8-hour CO NES have occurred, NES exceedences are mainly limited to PM₁₀. These exceedences occur regularly during the winter months, usually under calm meteorological conditions. Consequently, substantial monitoring and investigation of PM₁₀ has been conducted in Christchurch, with PM₁₀ explicitly targeted for management in the proposed NRRP. It is expected that measures targeting PM₁₀ will result in consequent reductions of PM_{2.5}.

3.3.2 Fine particle measurement and study

Particulate monitoring in Christchurch, has until relatively recently, focused on the measurement of the PM₁₀ size fraction. Although several air quality studies included measurement of PM_{2.5} (e.g. Wilton, 2003; Mikael *et al.*, 1999; Gunatilaka, 2000; Fisher *et al.*, 1998; and Scott, 2002), routine measurement of 24-hour PM_{2.5} concentrations did not commence until May 2001. Prior estimates indicated that on days when the PM₁₀ guideline of 50 $\mu\text{g m}^{-3}$ was exceeded, approximately 90% of measured particles were present as PM_{2.5} (Foster, 1998a). Since 2001, PM_{2.5} has been measured at Coles Place using a TEOM, fitted with a PM_{2.5} sampling head.

Several of the studies noted above also provided speciated measurements for PM_{2.5}. However, these studies did not focus specifically on 24-hour concentrations or supply sufficient data to provide adequate elemental representation of PM_{2.5} in Christchurch. Nevertheless, it is worth highlighting this research as it does provide valuable speciation information for different times of the day or year. Mikael *et al.* (1999) measured fine and coarse PM on 23 winter nights during the hours of 4 pm to 9 am; Gunatilaka (2000) provided 28 weekly samples of fine and coarse particles from April to October 1999; and Fisher *et al.* (1998) collected 21 PM_{2.5} samples for 4-hour time periods. Wilton (2003), conversely, provided some 24-hour measurements of PM_{2.5} and its key chemical constituents. The study was specifically targeted at addressing visibility and the measurements were conducted at an elevated location (on the top floor of a six-story building) at the Christchurch Polytechnic.

A preliminary source apportionment study of PM_{2.5} was conducted at the Coles Place monitoring site at St Albans during the winter of 2001 (Scott, 2002). These data, together with PM_{2.5} measurements collected by TEOM, indicated that like PM₁₀, PM_{2.5} concentrations were seasonally distributed, with low concentrations in the summer and substantially higher concentrations in the winter. The concentrations were frequently elevated during the winter months, with 38 exceedences of the MfE PM_{2.5} monitoring value of 25 $\mu\text{g m}^{-3}$ (24-hour average). The maximum PM_{2.5} concentration of 143 $\mu\text{g m}^{-3}$ occurred on 12 June 2001. These results confirm that PM_{2.5} is a significant air quality issue in Christchurch.

Major chemical constituents

Scott (2002) indicated that the major chemical species present in wintertime PM_{2.5} (May to August 2001) were OC and EC. OC concentrations were generally higher than EC and ranged from 1.9 $\mu\text{g m}^{-3}$ to 42.5 $\mu\text{g m}^{-3}$. The maximum EC concentration, conversely, was 28.2 $\mu\text{g m}^{-3}$. The peak concentrations occurred on the same day (1 June 2001), suggesting that these species were derived from similar sources or occurred under like meteorological conditions.

Inorganic ion species were also abundant in PM_{2.5}. Species measured included ammonium, nitrate and sulphate. Sulphate and nitrate were generally present at higher concentrations than ammonium.

Peak concentrations of these species occurred on different days, with maximums of $3.3 \mu\text{g m}^{-3}$ for sulphate, $2.3 \mu\text{g m}^{-3}$ for nitrate and $2.1 \mu\text{g m}^{-3}$ for ammonium.

Other elemental species of note included chlorine, sulphur, potassium and sodium. Maximum concentrations were $2.1 \mu\text{g m}^{-3}$, $1.5 \mu\text{g m}^{-3}$, $1.2 \mu\text{g m}^{-3}$ and $1 \mu\text{g m}^{-3}$, respectively. The peak potassium concentration occurred on the same day as maximum OC and EC. Potassium is a marker of wood smoke and its association with the carbon species suggested that residential heating was a major source of $\text{PM}_{2.5}$ on that day. Concurrently occurring maxima for sodium and chlorine were also evident indicating that marine aerosol was also likely to be a potential contributor to fine particles on certain days.

3.4 Major sources

The major contaminant emission sources in Christchurch have previously been identified by emission inventory techniques. Emission inventories identify sources and quantify the relative contributions of sources to emissions. In Christchurch, inventories of emissions to air were prepared for 1996 (NIWA, 1998), 1999 (Wilton, 2001a) and 2002 (Scott and Gunatilaka, 2004). Emissions were calculated for an "average winter's day"⁹ and contaminants inventoried include PM_{10} , $\text{PM}_{2.5}$, CO, CO_2 , NO_x , and oxides of sulphur (SO_x). In 2002, emissions from the Metropolitan Christchurch area (Christchurch City Council Territorial Boundary) were quantified and divided into three sub-areas: Inner Christchurch, Suburban Christchurch (encompasses Inner Christchurch), and Outer Christchurch (see Figure 3.7).¹⁰

The major source of PM_{10} emissions in Christchurch has consistently been identified as residential heating. The 2002 inventory (Scott and Gunatilaka, 2004) indicated that in Metropolitan Christchurch 82% of PM_{10} was derived from residential heating, 9% from industry and commerce, and 9% from motor vehicles.

⁹ In the home heating surveys, participants were asked about the main heating methods used on a "typical winter's day" or a "cold winter's day". It is the author's view that this represents average use, as a wood burner operation survey conducted in 2003 found that over 75% of households used their wood burners for five days or more per week (Lamb, 2003). Once householders start using their appliances in the winter, it is likely that they continue to use them regularly until the weather starts to warm up at the end of the winter season.

¹⁰ In 2005, the 2002 emission inventory data were revised by Environment Canterbury, due to the availability of better fuel use information. This effectively reduced the 2002 contribution from residential heating, and increased those from motor vehicles and industry (see examples of the revised estimates in Section 11.3.1). However, the figures quoted here are those reported by Scott and Gunatilaka (2004).

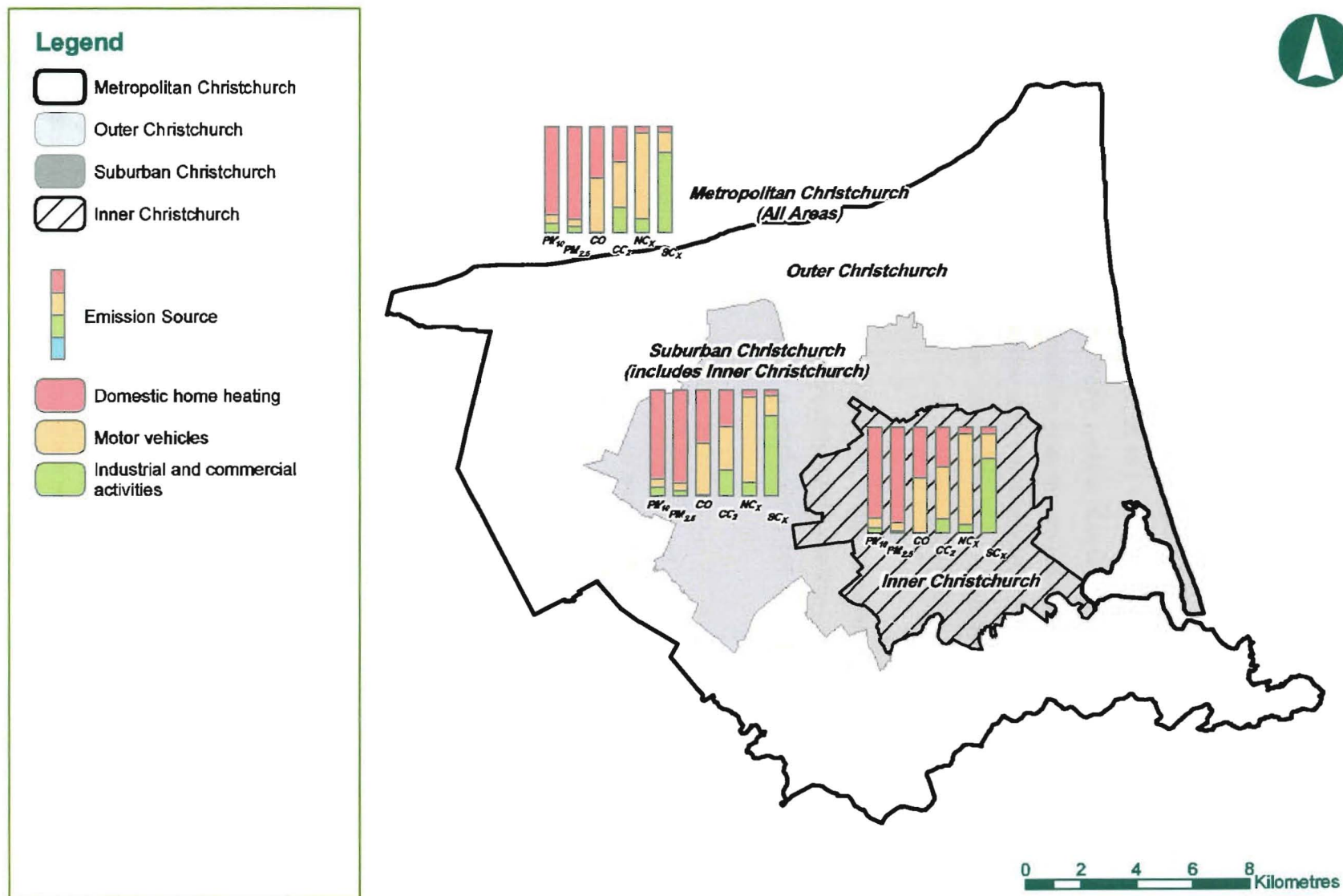


Figure 3.7 Relative source contributions (%) to contaminant emissions in Christchurch, 2002 (Scott and Gunatilaka, 2004).

A higher proportion of PM_{2.5} emissions were discharged from residential heating sources in Metropolitan Christchurch, with a contribution of 85%. Motor vehicle emissions contributed to 9% of PM_{2.5}, with 6% derived from industry and commerce. On a typical winter's day, residential heating emitted a total of 10 tonnes (t) of PM_{2.5}. Peak emissions occurred in the evening period between the hours of 4 pm and 10 pm. Wood burners, contributing 63% (6.5 t) of residential heating PM_{2.5} emissions, were the major source in this category.

As three inventories have been prepared for Christchurch, trends in emissions over time (1996 to 2002) could be determined. Scott and Gunatilaka (2004) found that PM₁₀ emissions in Metropolitan Christchurch decreased from 16 t in 1999 to 14 t in 2002 (-13%). Reductions were mainly from the residential heating (-15%) and motor vehicle sectors (-15%). The decline in PM₁₀ emissions was attributed to the tightening of wood burner emission standards over time, and increased publicity associated with the proposed NRRP. Reductions in motor vehicle emissions were ascribed to greater infiltration of improved engine technology into the motor vehicle fleet. Industrial and commercial emissions, conversely, appeared to be on the rise.

PM_{2.5} emissions were not quantified in earlier inventories, so trends in emissions could not be established. Nevertheless, as PM₁₀ emissions in Christchurch were dominated by combustion sources, which are also responsible for most PM_{2.5} emissions, it is highly likely that PM_{2.5} would also be declining.

While emission inventories provide a broad indication of the relative contribution of sources to emissions, they cannot determine contributions to actual measured concentrations. Air quality modelling is required to predict the impact of source emissions on concentrations. To address this issue, a chemical box model was modified and applied to the Christchurch situation by Gimson and Fisher (1997). The model simulated the influence of meteorological variables such as wind speed, air temperature and height of the mixing layer on contaminant emissions, thus allowing concentrations to be predicted.¹¹ Foster (1998b) applied the box model to 1996 inventory data and found that nighttime emissions had a greater impact on the 24-hour concentration than daytime emissions. The relative contributions from the different sources changed accordingly, from 82 to 90% for residential heating, 10 to 4% for transport and 8 to 6% for industry, as estimated by the 1996 inventory and box model, respectively (Foster, 1998b). These results, together with those obtained by Gimson and Fisher (1997) and Gimson (1998), confirm that emissions generated overnight during restricted dispersion conditions have a greater impact on concentrations than those discharged during the day.

¹¹ Box models are very simplistic and do not account for spatial variations in the distribution of emissions or in meteorology. Environment Canterbury plans to use an airshed model to provide a better representation of the interactions between contaminants and meteorology in Christchurch. Such models have already been advanced by the University of Canterbury (Zawar-Reza *et al.*, 2005).

3.5 Air quality management

Air quality monitoring and source assessments in Christchurch clearly indicate community health is at risk from fine particle pollution and that residential heating is the primary cause of elevated PM₁₀ and PM_{2.5}. Management action addressing these concerns is currently underway in the form of the Environment Canterbury's proposed NRRP.

Air quality issues are not new to Christchurch and management intervention has been necessary for many years. Air pollution was first publicly acknowledged as an issue in the 1860s when a press report of smoke nuisance was published. The primary air quality concern at that time, and in the ensuing years, was particle (or smoke) pollution. Various organisations have managed air quality in Christchurch including the Christchurch City Council, the Department of Health and the Canterbury United Council. In 1991, the Resource Management Act (RMA) was established which delegated responsibility for monitoring and managing the air resource to regional authorities. The responsibility for managing air quality therefore was transferred from the Department of Health to Environment Canterbury (previously known as the Canterbury Regional Council).

During the early years (1960s), air quality measures focused on emissions from industrial and commercial activities. By 1970, studies conducted by the Department of Health were suggesting that domestic open fires were a major source of smoke pollution. The Clean Air Act was established in 1972, providing for the development of Clean Air Zones. The Christchurch Clean Air Zones, subsequently established in 1975 and extended in 1984, prohibited the installation of new unapproved fuel burning equipment. Rules concerning the type of residential heating appliance and fuels used were eventually introduced, including the prohibition on open fire installations from 1982 (Environment Canterbury, 2002a).

Environment Canterbury, as part of its requirements under the RMA (1991), prepared a Regional Policy Statement (RPS). The RPS, which became operative in 1998, outlined the nature of the air quality issues facing the Canterbury region. It reiterated that air quality was an issue in Christchurch and that particle concentrations were exceeding ambient guidelines set by the MfE. Health and nuisance effects associated with combustion processes, odours and dust from agriculture, manufacturing and other industrial activities were identified as significant issues. The RPS outlined Environment Canterbury's intention to set ambient air quality standards and to maintain or improve air quality in Timaru and Christchurch (CRC, 1998). In order to achieve its policies, Environment Canterbury proposed the development of a Canterbury Natural Resources Regional Plan – Chapter 3: Air Quality (NRRP).

The proposed NRRP (Environment Canterbury, 2002b) was notified in June 2002, following an extensive consultation and review process. The air quality objective for PM₁₀ in Christchurch, as set out in the NRRP (AQL3) is:

"In the Christchurch Clean Air Zones 1 and 2, improve current poor winter air quality so that by the year 2012 there is a reduction in the concentration of PM₁₀ to less than 50 µg m⁻³ (24-hour average), with no more than one annual exceedence (averaged over three years), so as to reduce nuisance effects and adverse effects on human health".¹²

It has been estimated that 2002 PM₁₀ emissions must be reduced by 77% to meet this objective (Scott, 2005a). Accordingly, the plan places stringent requirements on discharges to air in Christchurch, and to a lesser extent on activities outside Christchurch (where similar goals apply). While the proposed plan imposes restrictions on many types of air discharges, emissions from residential heating are a particular focus. Table 3.3 outlines a selection of key rules contained in the proposed plan. Sources such as motor vehicles are not specifically targeted in the proposed NRRP, as a variety of strategies have been introduced at a national level to address motor vehicle emissions. Strategies supported by Environment Canterbury include the 10-second rule for smoky vehicles, the introduction of stricter motor vehicle emission criteria and the use of alternative forms of transport.

Air quality is also being addressed by central government. The Resource Management (National Environmental Standards relating to certain air quality pollutants, dioxins and other toxics) Regulations (2004) (NES) was recently promulgated by the Government, setting standards for criteria pollutants. The NES for PM₁₀ is:

50 µg m⁻³ (24-hour average), with one allowable exceedence per year, to be achieved by 2013.

The NES is particularly significant for Christchurch, as regulatory authorities in non-complying areas will no longer be able to issue new air discharge consents for sources of PM₁₀ from 2005, if a "resource consent is likely to cause, at any time, the concentration of PM₁₀ in the airshed to be above the straight line path" (MfE, 2004).¹³ As meteorological conditions vary, and planning processes are slow and a reasonable amount of time is required to allow air quality strategies to take effect, it is probable that at times concentrations will be above the straight line path specified for Christchurch.

¹² Clean Air Zone 1 defines the area of existing poor air quality in Christchurch, and Clean Air Zone 2 provides a buffer, recognising the contribution of emissions from this zone to air quality issues in Zone 1 (Environment Canterbury, 2002a). These are management zones and take into account those areas where potential development may impact on the central city. Conversely, the emission inventory areas focus on already established areas and are defined on a census area unit basis to facilitate data collection.

¹³ The straight line path "means a straight line that – (a) starts on the y axis of a graph at a point representing the extent to which the concentration of PM₁₀ in the airshed breaches its ambient air quality standard at 1 September 2005; and (b) ends on the x axis of the graph at a point representing the ambient air quality standard for PM₁₀ in the airshed at 1 September 2013" (NES, Regulation 17A).

Implementation of this standard is currently a vexing issue for resource management authorities in New Zealand.

If the straight line is defined using concentrations it will be necessary for reliable information concerning the relative contribution of sources to concentrations, rather than emissions, to be available. In addition, as regional authorities can only directly control primary anthropogenic emissions, it will be essential to take natural and secondary particulate contributions to measured concentrations into consideration when setting the start and end-points of the straight line. A greater understanding of the precursors and formative processes that lead to secondary particulate may also be needed.

Table 3.3 Summary of key rules in the proposed NRRP (adapted from Environment Canterbury, 2002b).

Christchurch urban area ¹⁴	Canterbury (excluding Christchurch urban area)
Residential heating	
<ul style="list-style-type: none"> Open fire use prohibited from 2006 (or operative date if after 2006)¹⁵ From 2008, high emission appliances must be replaced 15 years after installation date Only low emission burners can be installed (and only into homes that already use solid fuel for heating) No solid fuel burners to be installed in new homes from 2003 Restrictions on the type of materials burnt on domestic fires 	<ul style="list-style-type: none"> Only low emission burners can be installed Resource consent required to install an open fire Restrictions on the type of materials burnt on domestic fires
Industry	
<ul style="list-style-type: none"> Industries of a certain size and type require resource consent to discharge contaminants to air Industries must meet strict emission criteria 	<ul style="list-style-type: none"> Industries of a certain size and type require resource consent to discharge contaminants to air Industries must meet emission criteria
Outdoor burning	
<ul style="list-style-type: none"> Resource consent required to conduct outdoor burning on residential properties Restrictions on the types of materials that may be burnt Resource consent required to burn other types of materials 	<ul style="list-style-type: none"> Restrictions on the types of materials that may be burnt Resource consent required to burn other types of materials
Agrichemical spraying	
<ul style="list-style-type: none"> Concerned neighbours must be notified when spraying in proximity to property boundaries Restrictions on spraying in public parks No spray drift beyond the property boundary or into waterways. Training and certification requirements 	<ul style="list-style-type: none"> No spray drift beyond the property boundary or into waterways Concerned neighbours must be notified when spraying near the property boundary Training and certification requirements
Odour	
	<ul style="list-style-type: none"> No offensive or objectionable odours beyond property boundary Rules on intensive farming and waste management practices anywhere in Canterbury

¹⁴ Christchurch urban area in this instance refers to Christchurch Clean Air Zone 1 and 2.

¹⁵ Open fires may continue to be used in Clean Air Zone 2.

Nevertheless, it is important to work towards attainment of the NES (a reduction of 77% in 2002 PM_{10} emissions is required; Scott, 2005a) and ALQ3 of the proposed NRRP. Current emission forecasts are suggesting that attainment of these air quality targets may not be achieved within the required timeframes. However, these forecasts are reliant on specific assumptions (outlined in Scott, 2005a) and may change as more reliable information becomes available over time.

The proposed NRRP is not yet operational as the planning and review processes are still progressing. A hearing of submissions under the first schedule of the Resource Management Act (1991) is presently underway, and provisions addressed through the submission process may be subject to change. It is expected that the hearings will be completed later this year, a decision reached early 2006 and the plan become operative by 2008. Once operative, the success of the plan will need to be evaluated on a regular basis, and quantified where possible. Effective methods for measuring success will need to be developed. These methods will need to attribute improvements in concentrations directly to sources, so that the effectiveness of plan strategies targeting specific sources may be evaluated.

3.6 Summary

The meteorology and nature of source emissions in Christchurch are conducive to pollutant build-up on cold winter days. PM_{10} measurements currently exceed the recently established NES on a regular basis during the winter months. The major chemical constituents of $PM_{2.5}$ at that time are OC and EC. These chemical species are derived from anthropogenic combustion processes. Residential heating has been identified as the major source of these contaminants and has subsequently been targeted in the proposed NRRP. Substantial reductions in PM emissions are required to meet the objectives of the NRRP and the NES.

The proposed NRRP has yet to be finalised as review processes are still progressing. Once operative, the success of the plan will require evaluation. Methodologies will need to be adopted to indicate whether particle concentrations are decreasing and attribute declines to the relevant source sectors. This issue is the focus of discussion in the following chapters.

Chapter 4: Source identification and apportionment

There are two key methods used to identify sources and quantify their contributions to fine particle emissions or concentrations. These are emission inventories and receptor models. Emission inventories are widely used in New Zealand and will only be discussed briefly. The discussion will focus on a less well-used technique known as receptor modelling. The use of receptor models for source apportionment is relatively new to New Zealand. This study evaluates the ability of a receptor model to apportion fine particle mass in Christchurch and investigates its potential use as an air quality management tool.

4.1 Emission inventories

The most common method used by regulatory authorities, internationally, to identify pollutant sources and estimate relative contributions to emissions is an *emission inventory*. Emission inventories allow pollutant sources to be identified, quantified and subsequently targeted in emission control strategies.

An emission inventory, in its simplest form, follows the process summarised in Figure 4.1. A more detailed and comprehensive procedure is outlined in MfE (2001).

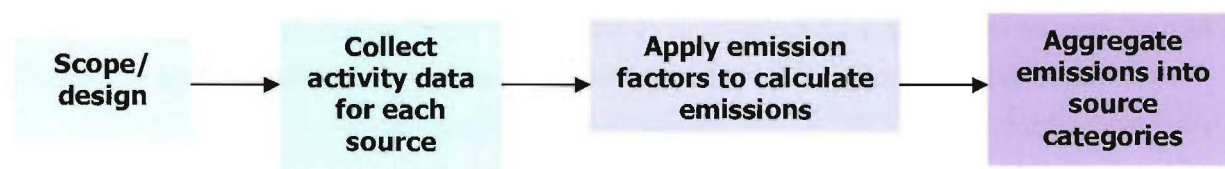


Figure 4.1 Emission inventory development (adapted from MfE, 2001).

As indicated, the first step involves setting the objectives and scope of the study. The area, contaminants and source categories must be selected and the desired temporal and spatial resolution defined. The second stage concerns the collection of activity data. Data should be compiled for all sources included in the inventory and classified by type of process or activity, and type and quantity of fuel used. Emission factors are then applied to the activity data to estimate the quantity of emissions provided by each individual source. These results are subsequently aggregated into the required source groupings to quantify relative contributions to total emissions within the study area.

There are a number of issues associated with emission inventories. These relate to both the data collection and emission calculation stages. These issues are outlined in the following section together with a brief discussion of the use of emission inventories as air quality management tools.

4.1.1 Collection of activity data

The collection of adequate activity data is crucial for reliable emission estimates to be obtained. The accuracy of these estimates is dependent on the quality, resolution and representativeness of the activity data. This issue became evident during the compilation of the 2002 Christchurch emission inventory (Scott and Gunatilaka, 2004). In 2002, industrial activity data were primarily collected by questionnaire and were supplemented, where required, with resource consent information.¹⁶ This provided detailed information and improved the ability of the inventory to differentiate between sources within a specific category. Collection of more comprehensive data allowed better differentiation between garnet and sand blasting in the abrasive blasting category, for example, which significantly impacted on calculated emissions (Scott and Gunatilaka, 2004).¹⁷ In a more general sense, if information collected for one sector is more detailed than another then this can lead to a potential bias in the emission inventory results.

4.1.2 Emission factors

Emission factors are representative values applied to activity data to provide a measure of contaminant discharge for a specific type of activity and fuel consumption. The USEPA has established an extensive database of emission factors known as the AP-42 (USEPA, 1995). The factors in the AP-42 database are averages of all available data of acceptable quality, and assumed to be representative of long-term averages for all facilities within a source category. These emission factors were derived using a combination of direct source measurements and continuous emission monitor data (where available). The measurements do not always include filterable and condensable particulate emissions, which can result in emissions being underestimated.

Although extensive datasets are available in the US to derive emission factors, they are not necessarily applicable to New Zealand due to differences in fuel composition and technology. MfE (2001) suggests that the uncertainty associated with emission factor data could be greater than five times the actual emission factor used for some processes.

Ideally, locally-derived emission factors should be used. To establish a suitable dataset though, would require significant funding and extensive emission testing. Localised emission testing, on a limited scale, is currently being conducted in New Zealand for residential heaters and motor vehicles, but there is no such programme in place to address industrial emissions. The emission factors in

¹⁶ In previous years, data contained in the resource consent files comprised the primary information source.

¹⁷ Garnet blasting has a substantially lower emission factor than sand blasting. If some garnet blasting activities are inadvertently classified as sand blasting then emissions can be overestimated.

current use in New Zealand, therefore, are associated with a reasonably high degree of uncertainty and are not necessarily representative of the range of New Zealand activities and fuels.

4.1.3 Application of emission inventories

Emission inventories are, nevertheless, valuable air quality management tools. Inventories identify the main sources contributing to contaminant emissions and can (depending on the inventory) provide a breakdown of the sub-sources within each category. This information allows air quality managers to identify problem sources and introduce measures to reduce emissions from those sources. Inventories can also assist with identifying previously unknown sources and highlight areas where air quality monitoring may be advisable. Emission trends may be established over time (provided that inventory methodologies between years are comparable), thus enabling the effectiveness of air quality strategies on emissions to be evaluated.

However, there are a number of limitations associated with determining source contributions by emission inventory. Firstly, emission inventories can only provide an approximate measure of the average contribution of various sources, as the estimates are based on averaged activity rate data or fuel consumption, and averaged emission rates (Stevenson, undated). Inventories cannot determine variations on a day-to-day basis. Secondly, emission inventories are not effective at quantifying biogenic or natural emissions. Marine aerosol and soil emissions are difficult to quantify using current inventory techniques, as robust activity rates are not readily available. Thirdly, and most significantly, source contributions to emissions are likely to differ from contributions to actual measured concentrations. Atmospheric processes including condensation, vaporisation, agglomeration and secondary reactions can significantly change the characteristics and concentrations of emissions subsequent to discharge. Dispersion or box models must be used in conjunction with emission data to relate emissions to estimated concentrations.

Although emission inventories are limited in scope and application, they are a vital source of information and are needed to determine and justify air quality strategies. However, additional tools are required to address the short-comings of emission inventories and to track progress towards the NES. Methods such as receptor models provide greater flexibility, can quantify natural and secondary contributions and attribute source contributions directly to concentrations on a daily basis. These techniques will be discussed in greater detail in the following sections.

4.2 Receptor modelling

4.2.1 Background

Source apportionment methods, that directly relate source emissions to quantitative impacts on measured concentrations, have been developed in recent years. Two methods are commonly used. The first is a prognostic mathematical modelling technique, known as a dispersion model, which takes atmospheric chemistry and physical processes impacting on emissions into account. These models

simulate pollutant transport and transformation from the point of emission to a receptor site where the pollutant concentration is predicted. Although used widely internationally, these techniques have been limited by the resources and time required to set-up and conduct the modelling. However, rapid advances in technology will allow them to be used routinely in the near future.

The second method, receptor modelling, is a cost-effective, diagnostic technique. It takes speciated concentrations measured at a receptor (or point of impact) and works in reverse to determine the contributions of sources to measured concentrations. The relationship between measured concentrations and emission sources is inferred, without the need for simulating dispersion processes, as the model works directly with concentrations rather than emissions. The information required to conduct receptor modelling is simply knowledge of the chemical composition of particulate concentrations at the source and receptor. Additional information such as meteorology, topography, location and magnitude of sources, while useful for interpretative purposes, is not vital (Seinfeld and Pandis, 1998). As modelling of these processes is not needed, analytical costs are significantly reduced. Nevertheless, a good understanding of local air quality processes is essential to allow factors resolved during the modelling to be appropriately interpreted and identified.

4.2.2 Principles of receptor modelling

Receptor modelling is defined by Main and Roberts (2001) as:

"a specified mathematical procedure for identifying and quantifying the sources of ambient air contaminants at a receptor, primarily on the basis of concentration measurements at that receptor."

The premise on which receptor modelling is based is that a contaminant concentration measured at a receptor is the sum of concentrations of that contaminant from all discharge sources, commonly known as the principle of mass conservation (Hopke, 1991). This is demonstrated in the following example where a 24-hour Iron measurement from Environment Canterbury's Coles Place monitoring site is the sum of:

$$Fe_{conc} = Fe_{motor\ vehicles} + Fe_{industry} + Fe_{soil} + \dots \quad [16]$$

The quantity of iron from motor vehicles (Equation 17), for example, is the sum of the proportion of iron in motor vehicle PM (a_{Fe}) multiplied by the mass concentration of all particles of motor vehicle origin (f). This is expressed as:

$$Fe_{motor\ vehicles} = a_{Fe\ Motor\ Vehicles} f_{Motor\ Vehicles} \quad [17]$$

In assessments of ambient air quality, receptor models are usually applied to matrices of chemically speciated data. The matrix of concentrations consists of m chemical species and n observations.

Receptor models, incorporating a mass balance approach, identify p sources and apportion $\text{PM}_{2.5}$ concentrations to those sources. The mass balance equation may be written as:

$$x_{ij} = \sum_{k=1}^p f_{ik} \cdot g_{kj} \quad (i=1, \dots, m, j=1, \dots, n) \quad [18]$$

Where:

x_{ij} = i th elemental concentration for the j th sample

f_{ik} = gravimetric concentration for the i th element from the k th source

g_{ik} = airborne mass concentration from the k th source contributing to the j th sample

There are two different categories of receptor models: single-sample and multivariate methods (Main and Roberts, 2001). Single-sample methods, such as chemical mass balance (CMB), require independent analyses to be performed on each available sample. Multivariate methods require multiple samples and simultaneously analyse correlations between measured concentrations of chemical species. Highly correlated species are assumed to be derived from the same source, and many samples are required for the analysis to provide valid source identification. Receptor models, depending on the model used, can provide chemical profiles for each source and apportion $\text{PM}_{2.5}$ concentrations to those sources on an observation (daily) basis.

Receptor models, like all source attribution tools, have a number of limitations. Firstly, receptor models assess source contributions at a single location. This is an issue if the receptor site is not appropriate for managing air quality in the area of interest. The site selected for this investigation, Coles Place, is located in the Christchurch suburb of St Albans. A description of the location and characteristics of the monitoring site is given in Chapter 6. Monitoring data from this site are used to indicate long-term air quality trends in Christchurch, and provided the basis for the proposed NRRP. Receptor modelling at a single location is not viewed as a significant limitation in this instance.

Receptor models, like emission inventories, are reliant on access to source profiles that are representative of source measurements observed at a receptor site. As indicated previously, the elemental composition of a source can change from point of discharge to measurement at a receptor. In recent years, emission testing (which provides source profile data) has generally been conducted to allow for contaminant transformation, by diluting samples with ambient air prior to testing. Nevertheless, access to source profiles is an issue, particularly in New Zealand where the availability of chemically speciated source profiles is limited. However, source apportionment can still be conducted successfully without a comprehensive source profile library, but requires a level of subjective judgement.

Receptor modelling is of limited benefit in areas where photochemically produced contaminants such as sulphates, nitrates and some organic compounds are a substantial issue. The primary emission sources associated with secondary particulate species cannot be determined by a receptor model

(Henry, 1991). If secondary particulate species are present in an area, a receptor modelling analysis tends to group species into a single secondary particulate source factor. While it is important to acknowledge these limitations, these issues are unlikely to have significant implications for receptor modelling in Christchurch.

The following sections discuss two different types of receptor models, CMB and multivariate, and outline the reasons for selecting the PMF receptor model for investigation.

4.2.3 Chemical Mass Balance (CMB)

The CMB approach was developed in the 1970s and used widely from the 1980s onwards, for air quality assessments. Detailed knowledge of the chemical and physical characteristics of gases and particles measured at both the source and receptor are required to identify sources and quantify their contributions to concentrations at a receptor site (Watson *et al.*, 1991). Source apportionment by CMB is conducted by solving a series of linear equations. Each equation represents receptor concentrations for each chemical species as a linear sum of products of source compositions and contributions. The solution is derived through inverse variance weighted least-squares linear regression (Watson *et al.*, 1990a,b as cited in Miller *et al.*, 2002). The model calculates contributions from each source, uses input data uncertainties to weight data as required and estimates uncertainties associated with the derived source contributions.

Critical to CMB is advanced, prior knowledge of the sources impacting on concentrations at a receptor site, and their chemical compositions. Consequently, a comprehensive emission profile database, encompassing all possible sources, is mandatory. While this is not an issue in the US where large datasets are readily available, it is a significant limitation in New Zealand, where different fuel types and technology are used. A comprehensive programme for collecting source profiles has not yet been conducted in New Zealand, and as such, few elemental profiles are available.

CMB applications are limited if the chemical composition of the contributing sources is not sufficiently distinctive. Co-linearity, where sources with similar fingerprints or a source whose profile is a linear combination of other source profiles, can reduce CMB's ability to adequately resolve sources. This is possible in Christchurch, where sources such as motor vehicles and residential heating have similar source profiles, and emissions behave in similar ways in response to meteorological influences.

Assumptions that apply to CMB, as detailed in Watson *et al.* (1991) and Schauer *et al.* (1996), include the following:

- The source emissions must be chemically stable and remain constant from emission to receptor.
- Individual chemical species must not be significantly depleted or increased through chemical processes (e.g. sulphate).

- All sources contributing to concentrations must be identified prior to conducting the analysis.
- The number of sources must be less than or equal to the number of chemical species included in the modelling.
- Measurement uncertainties are random, uncorrelated and normally distributed.

Due to the limited availability of locally derived elemental source profiles, CMB is not presently viewed as a viable receptor modelling method for Christchurch. Should a comprehensive source profile library become available in future years, use of this method could be reconsidered.

4.2.4 Multivariate methods

Multivariate models are based on the assumption that chemical species from the same source are correlated and that grouped correlations represent an emission source. These methods extract a number of *factors* (representing sources) from a speciated dataset, provide a chemical profile for each source (*factor loadings*) and indicate source significance on an observation (daily) basis using *factor scores*. Non-normalised scores may be regressed against PM_{2.5} mass to determine relative source contributions.

Several types of multivariate model are commonly applied to air quality data. These include factor analysis (FA), PCA, PMF, self modelling curve resolution (SMCR) and target transformation factor analysis (TTFA). The following discussion will focus on PCA and PMF.

Principal Components Analysis (PCA)

PCA, in its simplest form, transforms a complex matrix dataset (e.g. a chemical species concentration matrix) into a series of independent, mutually uncorrelated variables (known as *principal components*¹⁸ or *factors*). These components attempt to explain a maximum of the data variance, with most of the variance accounted for in the first component (Thurston and Spengler, 1985). The second component accounts for the maximum of the remaining variance and so on. A concentration measurement made at a receptor site is the linear combination of the *eigenvectors* or principal components.

The principal component solution is obtained by singular value decomposition of the data matrix (Jolliffe, 1986, as cited in Henry 1991). The matrix may be described as:

$$C = LF \quad [19]$$

where: C = a data matrix of m rows of species and n observations arranged in columns

L = the component loading matrix

¹⁸ Components are the eigenvectors of a variance-covariance matrix (Davis, 1973). When the data matrix comprises elemental concentrations by observations, the components represent elemental source profiles.

F = the matrix of component scores

PCA produces a matrix of elemental factor loadings, used to compile elemental profiles for each source, and factor scores, where each observation and factor is scored to indicate days when a particular factor or source is important. Key terminology encountered during a PCA is outlined in Table 4.1.

Table 4.1 Key principal components analysis terminology as applied to source apportionment.

Term	Description
Factor, principal component	In receptor modelling, a factor, principal component or eigenvector represents an emission source
Factor loadings	Correlation between a variable and a factor
Factor scores	Contribution of a factor to a particular case/sample
Squared loadings	Proportion of variance of each variable accounted for by the factor
Communality	Sum of squared factor loadings, so proportion of variance accounted for by each variable
Eigenvalue	Sum of the squared column loadings

Sources: Davis (1973), Goddard and Kirby (1976)

There are a number of assumptions and requirements that apply to PCA. As outlined in Seinfeld and Pandis (1998), these are:

- composition of the emission sources remain constant
- no interaction of chemicals, and concentrations are linearly additive
- variations in measurement are due to variations in concentration, rather than changing levels of uncertainty or source composition
- the effect of processes such as temperature inversions on all emissions is less than processes that affect individual sources
- a greater number of observations than sources is required
- eigenvector rotations are meaningful
- measurement errors are random and uncorrelated.

One of the limitations associated with PCA is that it only identifies the main patterns of variation present in a dataset. Initial components identified rarely make physical sense, as PCA includes most of the variance in the first factor. Additional transformation techniques, known as rotation, are usually required (Goddard and Kirby, 1976). Factor rotation maximises the number of factor loadings close to unity, redistributes variance amongst the factors and can provide more representative results. The data fit is not improved through rotation, although the solution is simplified (Kim and Mueller, 1978). However, rotation is not ideal as transformation methods do not necessarily produce physically meaningful data and negative source contributions may result (Henry, 1987; Lowenthal and Rahn, 1987). It has been claimed that no fully satisfactory rotation techniques have yet been derived (Ramadan *et al.*, 2000).

PCA is generally conducted on a normalised dataset. That is, each variable is transformed so that each chemical species has a mean of zero and a variance of one. This ensures that each species is considered equally and the results are not influenced by differences in units or the magnitude of concentrations. There are three significant limitations associated with normalising the data. Firstly, data scaling by row or column leads to distortions in the analysis and can obscure weak sources (Paatero and Tapper, 1993; Paatero and Hopke, 2003). Secondly, and more importantly, normalisation prevents quantitative source apportionment of particle mass without application of additional techniques (Hopke, 1991; Thurston and Spengler, 1985; Ames *et al.*, 2000; Henry, 1991). If the dataset is normalised then the loadings and scores are also normalised. The scores, while correlated with identified sources, are not proportional to source impacts (Thurston and Spengler, 1985). Normalising can also produce negative factor scores and loadings, which are not meaningful in a real-life situation as a source cannot make negative contributions.

Additional techniques have been developed that permit source attribution by PCA. In 1985, Thurston and Spengler proposed a method where *absolute principal component scores* were calculated and were regressed against PM_{2.5} mass to determine source contributions. The scores were non-normalised by including an extra "zero" day in the analysis. The limitations and lack of physical constraints associated with this method are well documented and are outlined in Henry (1987). An alternative apportionment approach may be to input the PCA source profiles into the CMB model.

Positive Matrix Factorisation (PMF)

PMF is a relatively new form of factor analysis developed by Paatero and Tapper (1994). Like PCA, PMF analyses a data matrix and identifies a series of independent factors. PMF conducts a least-squares analysis incorporating a data point weighting system to account for errors associated with individual concentration observations (Pollisar *et al.*, 2001). The data are not normalised and factor scores, output in real units, may be regressed directly against PM_{2.5} mass to obtain daily source contributions.

PMF, is essentially a weighted, constrained, least-squares fit technique. As detailed in Paatero (2000a), the model solves the following:

$$\text{Matrix equation:} \quad X = GF \quad [20]$$

Where X is known and G and F are unknown.

The equivalent equation in component form, including the residual matrix, is:

$$X_{ij} = \sum_{h=1}^p g_{ih} f_{hj} + e_{ij} \quad (i=1, \dots, m, j=1, \dots, n) \quad [21]$$

where X_{ij} = $m \times n$ data matrix

i = observation

j = element

m = number of chemical species

n = number of observations

p = number of factors

h = factor

$g = i \times h$ matrix with (p) factors and (n) observations

$f = h \times j$ matrix with (m) species and (p) factors

e_{ij} = residual matrix with m species and n observations

The analysis output includes an F-Factor and a G-Factor matrix. The F-Factor matrix is the equivalent of factor loadings, and the G-Factor matrix, of factor scores, in traditional FA/PCA.

The PMF model avoids the generation of negative factors and scores, which are not physically possible in air quality analyses, by minimising the "object function" $Q(E)$. This represents the sum of squares and is defined as:

$$Q(E) = \sum_{i=1}^m \sum_{j=1}^n (e_{ij} / \sigma_{ij})^2 \quad [22]$$

Where: σ_{ij} = standard deviation (uncertainty) matrix of m species and n observations

A full description of the mathematical framework of PMF2 and PMF3¹⁹ is outlined in Paatero and Tapper (1994) and Paatero (1997a and b).

The main advantage of PMF over FA/PCA type techniques is that PMF provides factor loadings and scores in real units. Loadings may be used directly to assemble elemental source profiles and the scores regressed against fine particle mass to quantify relative source contributions.

PMF, whilst a relatively new technique, is currently gaining in international significance. It has been reported as providing superior source resolution and quantification to other receptor modelling techniques (Huang *et al.*, 1999, Paatero and Tapper, 1993; Polissar *et al.*, 1998; Miller *et al.*, 2002).

The PMF receptor model incorporates a number of key features which enable source apportionment to be conducted more effectively. Firstly, PMF has the ability to individually weight data points. This recognises that data are not always of equal certainty, nor errors uniform. It allows more data to be retained in the analysis and reduces the influence of outliers and extreme values. Zero and below-

¹⁹ PMF2 was developed to analyse two-dimensional matrices and PMF3 to conduct a three-way analysis.

detection limit values may remain in the dataset, following substitution where required, increasing the number of sampling days²⁰ available for analysis. In many cases, measurable data are excluded from the analysis when they are below reliable detection limits. PMF, simply allocates higher levels of uncertainty to below detection limit data. Polissar *et al.* (1998), for example, reported that although greater than 80% of chlorine concentrations in the 1998 study were below detection limits, a good marine aerosol profile could still be derived. This may not have been achievable if 80% of data were removed from the analysis. PMF also requires a full dataset with no missing data.²¹ To meet this requirement, substitutions with more representative data and the allocation of appropriate uncertainty values is essential.

Whilst individual data weighting is a significant advantage, selection of appropriate weights poses some difficulties. It is important that weights accurately reflect the uncertainty of particular values and are not used to manipulate the analysis. The integrity of the assessment should not be compromised by deliberately weighting data, based on prior assumptions regarding potential sources, so that elements become correlated. Allocated uncertainties should reflect the quality and quantity of each data point. PMF has a built-in function (FKEY), which adjusts concentrations for specified sources. This, in effect, influences the analysis and is considered acceptable provided that the details and justification for doing so are fully reported (Paatero, 2002b).

A prescribed data substitution and uncertainty allocation method must be selected in advance and applied consistently to the data. Although the actual method adopted is largely at the discretion of the user, approaches based on analytical measurement uncertainties and detection limits are commonly used. The approach outlined by Polissar *et al.* (1998) and implemented by Kim and Hopke (2003), Maykut *et al.* (2003), Hopke and Song (undated), Ramadan *et al.* (2000), where various combinations of analytical measurement uncertainties, detection limits and geometric mean concentration values were used, was adopted for this study.

Another important feature of PMF is the application of non-negativity constraints on the analysis. This allows physical realities to be maintained in the assessment, as a source cannot make negative contributions to fine particle mass. PCA, on the other hand, often produces negative factor loadings and scores, which have no basis in the physical world. These constraints are applied by a penalty function, which is proportional to the square of the negative value. Positive component values reduce the penalty function to a minimum, whereas a negative value increases the penalty coefficient to a maximum value (Paatero and Tapper, 1994). The uncertainty estimates σ_{ij} are iteratively re-weighted during the analysis to maintain non-negativity whilst minimising the sum of squares (see Equation 22).

²⁰ Values must be available for every element and observation for a sampling day to be included in the analysis.

²¹ Negative values may remain in the dataset if they result from noise in the data.

Outliers are also addressed by the PMF receptor model. These values are common in air quality datasets and, although the outliers are likely to be valid, distortions of the analysis can occur when methods such as PCA are used. PMF possesses a *robust mode* which may be activated to reduce the influence of outliers on model output. Higher levels of uncertainty are allocated to these data points.

Another useful function built into the PMF model is the *goodness of model fit function Q*, or *Chi-2 value*. This value helps determine the correct number of factors to use in the modelling. If there are no outliers and the uncertainty allocation is appropriate, this value should approximately equal the number of measurements in the data matrix. If the Q value is significantly different from the number of measurements in the matrix, then it is likely that the number of factors selected is incorrect.

Finally, PMF provides a peaking parameter (*f_{peak}*) for data rotation purposes. Multiple solutions are possible if the G-Factor data points are some distance from the coordinate axes. A "unique" solution is said to exist if values attempt to become negative during rotation (Paatero *et al.*, 2002). Unlike PCA, PMF conducts rotations simultaneously during the least-squares fitting process. The fit is continuously adjusted so that the factor elements remain non-negative. The Q-value increases in this instance (Paatero, 2000a).

Overall, PMF appears to contain a number of valuable features and allows a more complete source apportionment to be conducted. It has the ability to resolve key sources and directly apportions fine particle mass to those sources. It is cost-effective and has been reported to produce more effective source apportionment than other receptor modelling techniques (Miller *et al.*, 2002; Huang *et al.*, 1999; Paatero and Tapper, 1993; Polissar *et al.*, 1998). On this basis, the PMF receptor model has been selected for evaluation during this study.

4.3 Summary

There are a number of methods available for identifying sources and their contributions to fine particle emissions or concentrations. These include emission inventories and receptor models. Although emission inventories are limited in scope and application, they are vital for determining and justifying air quality strategies. Additional tools, such as receptor models, are required to address the short-comings of emission inventories and to track progress towards the NES. Receptor models provide greater flexibility, can quantify natural and secondary contributions and attribute source contributions to measured concentrations on a daily basis.

Receptor models available include CMB and multivariate methods. CMB requires comprehensive prior knowledge of the chemical composition of all sources. A library of such profiles is not presently available in New Zealand, rendering this method unsuitable. Multivariate methods reviewed include PCA and PMF. PMF is superior to PCA as it has the ability to individually weight data, maintains physical realities, minimises the influence of outliers, and provides factor loadings and scores in actual

units, thus allowing source apportionment to be conducted directly. This model will be used to conduct a source apportionment analysis of $PM_{2.5}$ data in Christchurch and the output provided by the model will be evaluated.

Chapter 5: Receptor model application

Prior to conducting source apportionment analyses using the PMF receptor model, it is useful to review similar research undertaken elsewhere. The PMF receptor model has been applied to air quality data in numerous studies overseas, but has yet to be used in a published New Zealand study. In New Zealand, techniques such as FA and PCA are generally used. This chapter will summarise source apportionment work conducted in New Zealand, and outlines a selection of international studies where the PMF receptor model was used. Of greatest interest, are the sources resolved by these studies and the chemical species characteristic of each source. This information is used by this study to interpret the resolved factors (see Chapter 9).

5.1 New Zealand studies

Source apportionment of PM by receptor modelling is a relatively new field of research in New Zealand. It was initiated in 1996, with the commencement of a speciation monitoring programme in Wellington. Since that time, receptor modelling has increased in popularity, with speciated measurements conducted in cities such as Hamilton, Nelson, Auckland and Christchurch. Source apportionment results obtained using the PCA and FA receptor models have been published for Wellington (Trompetter *et al.*, 2000; Davy *et al.*, 2002a,b), Hamilton (Senaratne, 2003), Auckland (Senaratne, 2003; Wilton, 2002; Stevenson, 2002) and Christchurch (Wilton, 2003; Senaratne, 2003). The following discussion will focus primarily on source apportionment conducted in Wellington and Christchurch.

5.1.1 Wellington

The elemental composition of PM_{2.5} and PM_{10-2.5} is routinely monitored in the Wellington Region using a GENT²² stacked filter unit. The filters are analysed at the Institute of Geological and Nuclear Sciences (GNS) using the Proton Induced X-Ray Emission (PIXE) technique. Currently, samples are collected for 24-hour durations, although previously measurements were conducted over two to four days. Speciated monitoring has been carried out at Baring Head (a pristine site at the southeastern entrance of Wellington Harbour), a rural site (20 km southeast of central Wellington), Huia Pool (an urban site in Lower Hutt), Upper Hutt (urban residential site), the Mt Victoria Tunnel (road tunnel) and Masterton (urban residential site). Source identification and apportionment of the elemental data has been conducted by Trompetter *et al.* (2000) and Davy *et al.* (2002a,b) using the multivariate FA technique.²³

²² GENT samplers were designed by the University of Gent, Belgium (under contract to the International Atomic Energy Agency (IAEA)).

²³ The source apportionment of Masterton data is ongoing and has not yet been published.

These studies present the elemental source profiles for each resolved factor and, in some instances, conduct source apportionment using the FA factor scores. The profiles were obtained by selecting a sample considered to be “uniquely” representative of a particular source, and reporting the proportional abundance of each elemental species on that day. Source apportionment was then undertaken using the normalised factor scores. However, there are two limitations to this approach. Where urban PM is collected over several days, it is more difficult to obtain a sample solely comprised of PM from a single source.²⁴ Secondly, the use of normalised factor scores to calculate source contributions is not ideal. The entire dataset, loadings and scores are normalised and the scores, while correlated with identified sources, are not proportional to source impacts (Thurston and Spengler, 1985). Nevertheless, the Wellington studies provide a valuable indication of sources that may be resolved by receptor modelling, and the elemental species characteristic of each source in New Zealand.

Table 5.1 presents the key elemental species found in sources resolved in and around Wellington. Five factors were obtained for Baring Head and the rural site, three factors for Upper Hutt, and four factors for the Mt Victoria Tunnel. These were identified as a variety of natural (sea salt and soil) and anthropogenic (smoke, industry and various motor vehicle components) sources. The results from the Mt Victoria tunnel were particularly useful as these were the first published elemental profiles representing composite motor vehicle emissions in New Zealand (i.e. composed of a mixture of motor vehicle types). The studies found that smoke source contributions at Baring Head and the rural site were high in winter (residential heating and biomass burning were likely sources) and low in summer, soil contributions at Upper Hutt were greatest during the summer months, and sea salt was also generally higher in summer, although some events occurred in winter. Overall, the results correspond with what would be expected of these sources on a seasonal basis. Further work programmed for the Wellington region includes source apportionment of PM_{2.5} and PM_{10-2.5} in Masterton using the PMF receptor model.

²⁴ This would depend on the identification of the resolved factors. If a single “combustion” factor is resolved, rather than separate wood combustion and motor vehicle factors, then it is quite possible that a sample primarily comprised of combustion PM would be available.

Table 5.1 Major sources contributing to PM_{2.5} in Wellington (PCA factor loadings; Trompetter *et al.*, 2000; Davy *et al.*, 2002a,b).

[illegible]

5.1.2 Christchurch

Christchurch haze study

In 1996, the National Institute of Water and Atmospheric Research Ltd (NIWA) was commissioned by the former Canterbury Regional Council (now Environment Canterbury) to investigate the nature and sources of particles contributing to haze in Christchurch (Fisher *et al.*, 1998). Fine particle samples (16 in total) were collected using an ANSTO²⁵ sampler at Opawa and Packe Street, during the winters of 1996 and 1997. Source apportionment analyses were attempted by the PCA and CMB receptor models, but the modelling was unsuccessful owing to the small number of samples collected and the lack of local source profile information. Consequently, the results will not be discussed in this report (refer to Fisher *et al.*, 1998).

Visibility degradation study

Speciated PM_{2.5} data have been collected in Christchurch on a periodic basis since 2000. The initial measurements were conducted as part of a visibility degradation study (Wilton, 2003). The study investigated the physical and chemical factors contributing to visibility reduction in Christchurch and conducted a source apportionment analysis to identify and quantify sources contributing to impaired visibility.

Fine particles were measured over a period of seven hours (0600-1300 hours) at the Christchurch Polytechnic site,²⁶ with a total of 250 valid samples collected. A Spiral Aerosol Speciation Sampler (SASS) collected the samples, which were subsequently analysed for elements (by PIXE) and ions (by Ion Chromatography (IC)). The PCA receptor model was applied to the speciated dataset to identify sources contributing to PM_{2.5} mass. The derived source profiles are outlined in Table 5.2.

A similar methodology to that adopted by Greater Wellington was used to construct the source profiles. A number of samples considered representative of a particular source were selected and the elemental species averaged to calculate the relative elemental abundances. The contributions of each source to mass were then calculated using a “unique element” approach.²⁷ However, zinc and iron were the “unique” elements used, which is not ideal, as these are derived from multiple sources (e.g. soil, motor vehicles, wood combustion).

²⁵ The ANSTO sampler was developed by the Australian Nuclear Science and Technology Organisation.

²⁶ Measurements at the Polytechnic site were conducted at the top of a six-story building. The site is located in a commercial area, close to the CBD at the junction of two major roads.

²⁷ An element considered unique to a source was selected. For each filter, the unique element was used to calculate the contribution of the source to total particulate by multiplying it by the inverse proportional contribution of that element to the source profile (Wilton, 2003).

Table 5.2 Major sources contributing to PM_{2.5} at the Christchurch Polytechnic (factor loadings; Wilton, 2003).

	Soil	Sulphates/ nitrates	Burning (Zn)	Burning (Fe)	Sea salt	Ni/ industry
Mg	0.88					
Al	0.80					
Si	0.69					
Na	0.52					
NO ₃ ⁻		0.96				
Cl ⁻		0.94				
SO ₄ ²⁻		0.93				
Zn			0.71			
NH ₄ ⁺			0.66			
Sc			0.56			
EC			0.52	0.61		
S				0.77		
Fe				0.74		
K				0.65		
Ca					0.85	
Cl					0.53	
Mn						0.74
Ni						0.72

Nevertheless, a six-factor solution was derived by the analysis and the factors identified as soil, secondary particulate, residential heating (Burning Zn), motor vehicles (Burning Fe), sea salt and an industrial nickel source. It was suggested that motor vehicles and secondary particulate were the main sources of daytime particle mass, and that residential heating was significant at times during the winter months (Wilton, 2003). Intuitively, the results of the study make sense. It is highly probable that during the morning hours, motor vehicles and secondary particulate are primary sources of PM_{2.5} at that monitoring location. Fresh emissions discharged during morning peak-hour traffic are exposed to UV light, resulting in a substantial increase in the number of nucleation-mode secondary particles.

Preliminary source apportionment study

Prior to commencing the current study, a preliminary chemical characterisation and source apportionment analysis was conducted during the winter of 2001 (Scott, 2002; Paterson, 2002). Air quality samples were collected from May to August on a 24-hour basis using a SASS. The samples were analysed for elements (using PIXE) and ions (using IC). The PMF receptor model was applied to the speciated dataset by Paterson (2002). A seven-factor solution was obtained and the sources were identified as secondary particulate, motor vehicles, sea salt, soil, wood burning, and two industrial sources. The factor loadings in ng m⁻³ are presented in Table 5.3.

The contributions of each source to PM_{2.5} were estimated by direct regression of the non-normalised factor scores against fine particle mass. Contributions to average PM_{2.5} were 68% from wood burning, 11% from secondary particulate, 8% from motor vehicles, 4% from sea salt, 4% from soil,

3% from Industry 1 and 2% from Industry 2. However, this study was limited in terms of data availability and the questionable nature of the OC and EC measurements.²⁸ Nevertheless, the investigation demonstrated the types of sources that may be resolved using the PMF receptor model, and the relative contributions to concentrations.

Table 5.3 Preliminary investigation of major sources contributing to 24-hour average PM_{2.5} (ng m⁻³) in Christchurch, winter 2001.

	Secondary PM	Motor vehicles	Sea salt	Soil	Wood burning	Industry 1	Industry 2
NH ₄ ⁺	0.38				0.02		
Cl ⁻			0.39		0.55		
NO ₃ ⁻	0.52	0.32					
SO ₄ ²⁻	0.49	0.35					
EC		2.80			5.18		
OC_adjusted		3.59			9.28		
Na			0.18				0.13
Mg			0.03				0.03
Al				0.04		0.02	
Si				0.14	0.03		
S	0.14				0.15		
Cl			0.29		0.29		
K					0.333		0.0336
Ca			0.0152				0.0109
Cr					0.00387	0.0159	
Fe					0.0345	0.0396	
Zn					0.00502		0.0463
PM _{2.5}	5.61				36.5		

NB: OC_adjusted = organic carbon converted to organic mass

5.1.3 Other New Zealand studies

A study of PM₁₀ and its chemical constituents was undertaken in Auckland during August, September and October 2001. Samples were collected for analysis of the ¹⁴C isotope and chemical elements by PIXE. The ¹⁴C data were used to distinguish between carbon discharged by fossil fuels (predominantly motor vehicle emissions) and more recent carbon sources such as firewood. The results were analysed using a non-traditional source apportionment technique and are presented in Stevenson (2002). Wilton (2002) reanalysed the Auckland data using PCA. Only three factors were resolved which were identified as combustion, sea spray and potassium iodide.

Senaratne (2003) conducted a source apportionment of air quality data collected in Auckland, Hamilton and Christchurch. Samples were collected for different time periods, size fractions and seasons, and analysed using PIXE and inductively coupled plasma/mass spectrometry (ICP/MS). Source identification was conducted using PCA and apportioned by absolute principal components analysis. Major sources of PM were identified as sea spray, suspended soil/road dust, domestic emissions, diesel and petrol vehicles.

²⁸ These issues are the same as those discussed in detail in Chapter 8.

5.2 International studies

Receptor models have been used internationally to conduct source apportionment of PM data for many years. The literature includes numerous studies where techniques such as CMB (e.g. Chen *et al.*, 2001; Klinedinst and Currie, 1999; Schauer *et al.*, 1996; Park *et al.*, 2001; Chow *et al.*, 1996a and Cohen, 1999), FA (Castanho and Artaxo, 2001; Kavouras *et al.*, 2001, Ames *et al.*, 2000), and PCA (Thurston and Spengler, 1985; Katrinak *et al.*, 1995) have been used. This chapter will focus only on those studies where the PMF receptor model has been applied.

PMF has been used for a variety of air quality applications, including assessments of arctic aerosol (Xie *et al.*, 1999), daily precipitation data (Juntto and Paatero, 1994) and indoor/outdoor exposure data (Yakovleva *et al.*, 1999). The following section will briefly summarise eight studies where PMF was used to apportion 24-hour average PM_{2.5} to various sources. Table 5.4 outlines key details of the eight studies reviewed. The studies evaluated were all based in the US and Canada, and sources contributing to PM_{2.5} concentrations at a range of rural and urban sites were identified. Study locations included Seattle, northwest Alaska, Phoenix, Vermont, Washington DC, Brigantine, Toronto and Atlanta. In most cases, large datasets of speciated PM_{2.5} were available for analysis (ranging from 289 to 981 samples). The PMF receptor model was applied to the data and eight to eleven factors were resolved by each study.

Similar sources were resolved in all studies, with some variation relating to specific sources located in close proximity to the monitoring site. Common sources included motor vehicles, secondary particulate, industries, soil and road dust. Additional sources resolved were wood smoke, marine aerosol (fresh and aged) and organic acids. Profiles were generally presented in a graphical form and actual factor loadings data were not provided. Details of these profiles are presented in Chapter 10, under the relevant source headings. However, a brief discussion is included below.

In studies where various OC and EC fractions were measured, motor vehicles were separately resolved into the petrol and diesel-fuelled vehicle categories. Motor vehicle contributions were usually local in origin, although in Vermont contributions from Canadian motor vehicles were detected (Polissar *et al.*, 2001). Typically, petrol and diesel vehicles were characterised by carbon compounds (OC and EC), metals such as zinc and iron, and soil-related elements (including silicon and calcium). Differentiation of the sources into the petrol and diesel categories was dependent on the ratios of different OC and EC fractions.²⁹ OC was higher relative to EC for petrol vehicles, while the reverse was true for diesel vehicles.

²⁹ Up to four OC and three EC fractions may be measured using techniques such as Thermal Optical Reflectance (TOR). This is one of the most common analytical techniques used to analyse carbon in PM samples.

A variety of industrial sources were resolved by these studies. These included fuel oil and coal combustion, incinerators, smelters (e.g. non-ferrous smelting), metal processing and cement kilns. As a general rule, fuel oil sources were distinguished by the presence of nickel and vanadium, coal combustion by selenium and sulphur, and incinerators by copper, lead and iron. Smelters and metal processing PM varied in accordance with the actual metals produced/used (e.g. zinc, aluminium, iron or copper) and the cement kiln discharges were characterised by carbon compounds and calcium.

Natural sources, such as marine aerosol and soil, were readily resolved by the PMF receptor model. Chemical species commonly associated with soil sources included sulphur, silicon, iron, potassium, magnesium, calcium, zinc, aluminium and titanium; and marine aerosol was characterised by the presence of sulphur, chlorine, potassium, magnesium and sodium. A source profile comprising sodium, sulphate and, sometimes, black carbon, was resolved by several studies (Polissar *et al.*, 1998; Polissar *et al.*, 2001; Maykut *et al.*, 2003). Identification of this source was vague, but Polissar *et al.* (1998) suggested it may represent a long-range transportation source, where sulphur species generated at some distance reacts with NaCl (from marine aerosol) to produce sulphate. This had led to labels such as "aged sea salt" being allocated to this source (Kim *et al.*, 2004b).

Wood combustion sources were resolved in most of the reviewed studies. The exceptions were Kim and Hopke (2003) and Lee *et al.* (2003). Sources grouped together as wood combustion were those identified as vegetation and biomass burning, forest fires and wood smoke. The elemental species most consistently identified were OC, EC and potassium. Other species sometimes included in the wood combustion profiles were zinc, calcium and sulphur (each identified in three of the studies), iron and silicon (in two studies), and chlorine, ammonium and nitrate (in one study).

Secondary particulate sources were resolved in most areas and varied depending on whether individual secondary species were resolved into separate factors. In some instances, there were several sulphate sources identified (e.g. Kim and Hopke, 2003 and Kim *et al.*, 2004a). These factors were characterised by the secondary species in question (or various combinations of sulphate, nitrate and ammonium), and often OC and EC were also present.

Table 5.4 Selection of studies where PMF receptor models have been applied to PM_{2.5} (Maykut *et al.*, 2003; Polissar *et al.*, 1998; Ramadan *et al.*, 2000; Polissar *et al.*, 2001; Kim and Hopke, 2003; Song *et al.*, 2001; Lee *et al.*, 2003; and Kim *et al.*, 2003b).

Study	Location	Number of samples	Identified sources	Comments and key features
Maykut <i>et al.</i> (2003)	Seattle, USA	289	<ul style="list-style-type: none"> - Gasoline - Diesel - Vegetative - Fuel oil - Soil - Marine - Na-rich - Secondary 	<p>The study divided EC and OC into seven temperature resolved fractions. The UNMIX, PMF and CMB receptor models were evaluated and compared. All three receptor models predicted that the major sources were vegetative burning (including wood stoves), mobile sources and secondary particles, with some soil and salt spray. PMF and UNMIX were able to resolve a fuel oil combustion source as well as distinguish between diesel emissions and other mobile sources. The results from these models correlated well with inventories.</p> <p>Summary of results:</p> <ul style="list-style-type: none"> • A seasonal effect was evident in contributions from vegetation burning and secondary sulphate sources. • A strong day of week influence was found in contributions from diesel and vegetative burning. • Average source contributions were vegetative burning (28%), diesel vehicles (18%), gasoline vehicles (4%), mobile sources (22%), fuel oil (10%), soil (14%), sea salt (3%), Na rich (5%) and secondary sulphate (18%).
Polissar <i>et al.</i> (1998)	Study presented results for several sites. Only the results for the Northwest Alaska areas are outlined.	491	<ul style="list-style-type: none"> - Sea salt - Soil dust (I) - Soil dust (II), coal combustion - Forest fires, local combustion - Incinerators, smelters - Motor vehicles, smelters - Distant anthropogenic (I) - Distant anthropogenic (II) 	<ul style="list-style-type: none"> • The calculated Q values were higher than theoretical Q by a factor of 1.5 to 3.5 • Soil sources peaked during the summer months. • The presence of black carbon in the sea salt factor suggested mixing of sea-salt and anthropogenic aerosol during transport. • The sources labelled distant anthropogenic both contained sulphur.

Study	Location	Number of samples	Identified sources	Comments and key features
Ramadan <i>et al.</i> (2000)	Phoenix, USA	Two datasets were collected: 981 & 217 samples. Only the larger dataset will be discussed.	<ul style="list-style-type: none"> - Biomass burning - Wood burning - Motor vehicles - Non-ferrous smelting - Heavy duty diesel - Sea salt - Soil - Secondary aerosol 	<ul style="list-style-type: none"> • The biomass and wood burning source contributions were higher in winter (some summer peaks evident). • Motor vehicle contributions were greatest during winter. • The aged sea salt source was aged in nature due to distance from the coast. • The secondary (coal-fired power plant) contributions were higher in the summer (coinciding with photochemical activity). • The greatest contributors to PM_{2.5} were motor vehicles, vegetation burning and secondary factors; sea salt was the least significant.
Polissar <i>et al.</i> (2001)	Vermont, USA	853	<ul style="list-style-type: none"> - Salt - Na-S - Canada-smelting - Cu smelting - Soil - Canada-Mn - Zn-Pb - Mid-West S-coal - East Coast oil - Mid-West W-coal - Wood smoke 	<ul style="list-style-type: none"> • The wood smoke contributions were highest in the winter (some summertime peaks). • Two coal-fired power plants were identified, where one peaked in the summer and the other in winter. • Oil-fired power plant contributions were greatest in winter/spring. • The Zn-Pb industrial source peaked in winter. • Contributions from Canadian sources were detected. • Soil contributions were greatest in summer. • The salt source comprised marine aerosol and salt from road-salting activities. • Both the salt source and Na-S source contributions were highest in winter/spring.
Kim and Hopke (2003)	Washington DC, USA	718	<ul style="list-style-type: none"> - Secondary sulphate I - Secondary sulphate II - Secondary sulphate III - Secondary nitrate - Gasoline vehicles - Incinerator - Aged sea salt - Airborne soil - Diesel emissions - Oil combustion 	<ul style="list-style-type: none"> • Temperature resolved carbon fractions were used in the receptor modelling. • Secondary sulphate I contributed 43% of PM_{2.5} mass, 11% was from secondary sulphate II, 6% from secondary sulphate III, 21% from gasoline vehicles, 2% from diesel vehicles, 9% from secondary nitrate, 4% from incinerators, 2% from sea salt, 2% from soil, and 2% from oil combustion. • The secondary sulphate I source had higher contributions in summer while sulphate III peaked in the winter. • Nitrate concentrations were highest in the wintertime. • The soil source contributions were greatest during the dry summer months.

Study	Location	Number of samples	Identified sources	Comments and key features
Song <i>et al.</i> (2001)	Data collected for various sites. Only Brigantine, USA is presented.	682	<ul style="list-style-type: none"> - Secondary sulphate - Coal combustion - Oil combustion - Soil - Incinerator - Sea salt - Nitrate - Motor vehicle - Wood smoke 	<ul style="list-style-type: none"> • All sources except for secondary sulphate and soil were higher on average during the winter. • The motor vehicle emissions did not change significantly throughout the year.
Lee <i>et al.</i> (2003)	Toronto, Canada	367	<ul style="list-style-type: none"> - Secondary coal - Ammonium nitrate - Vehicles/road dust - Vehicles/NaCl - Organic acids - PM primary 1 - Smelter - PM primary 2 	<ul style="list-style-type: none"> • Motor vehicle emissions were estimated to constitute 40% of the PM_{2.5}. In summer, secondary organic aerosols contributed ~20% of PM_{2.5}. • The inclusion of organic acids improved the source profiles. • The secondary coal factor comprised coal-fired power plants (long range transport). The contributions were greatest in summer than winter. • Ammonium nitrate originated from the west. It was suggested that in addition to ammonium availability, particulate nitrate was more significant when there is less sulphate available to react with ammonium. Contributions from this source were greatest during the winter months. • Vehicles/road dust refers to local traffic and includes dust emissions. • Vehicles/NaCl were more important in the winter and were associated with the de-icing of roads. • Organic acids were more significant in summer than in the winter (influenced by photochemistry). • The remaining sources were relatively minor. • A wood combustion source was not resolved, contrary to emission inventory findings.

Study	Location	Number of samples	Identified sources	Comments and key features
Kim <i>et al.</i> (2003b)	Atlanta, USA	529	<ul style="list-style-type: none"> - Sulphate-rich secondary aerosol I - On-road diesel emissions - Nitrate-rich secondary aerosol - Wood smoke - Gasoline vehicles - Sulphate-rich secondary aerosol II - Metal processing - Airborne soil - Rail-road traffic - Cement kiln/carbon-rich - Bus maintenance facility/highway traffic 	<ul style="list-style-type: none"> • Sulphate-rich secondary aerosol I (50% of $PM_{2.5}$) and II (7%) had higher concentrations during the summer months. • Four different traffic related sources were resolved – gasoline vehicles accounting for 6% of $PM_{2.5}$, on-road diesel (11%), railroad traffic (3%) and bus maintenance facility/highway traffic (2%). • Nitrate-rich secondary aerosol had maximum concentrations during the winter months suggesting that low temperatures and high humidity contribute to nitrate formation. Accounts for about 9% of $PM_{2.5}$. • Wood smoke contributed to 7% of $PM_{2.5}$ and was higher in winter than in the summer. Short-term peaks, however, were evident in spring and summer. • Metal processing (3% of $PM_{2.5}$) had higher contributions during the winter. • Air-borne soil (3% of $PM_{2.5}$) contributions were from the southwest and mainly during the dry summer season. Lower weekend contributions were interpreted as indicative that resuspended road dust was included in this factor. • Cement kiln/carbon-rich source (2% of $PM_{2.5}$) influenced by a kiln located 7 km northwest of the site. A seasonal pattern was not demonstrated and contributions were greatest on week-days.

5.3 Summary

A number of source apportionment studies have been conducted in New Zealand in recent years. These include investigations in Wellington, Auckland, Hamilton and Christchurch. Receptor modelling has generally been conducted by PCA and FA, and a variety of methods employed to determine relative elemental abundances for each factor and the source contributions. These studies provide valuable information with regard to the key elemental species present in the profiles of sources including marine aerosol (sea salt), soil, industry, smoke and motor vehicles. The findings of these studies will be useful in the identification of sources contributing to fine particles in Christchurch.

The international studies discussed, conducted source apportionment of $PM_{2.5}$ using the PMF receptor model. PMF was able to successfully resolve the main sources of $PM_{2.5}$ including marine aerosol, industrial sources (smelters, incinerators, coal combustion and metal processing), diesel and petrol-fuelled motor vehicles, secondary particulate and wood combustion. These profiles, presented in Chapter 10, are used to interpret source profiles resolved for Christchurch by this study.

Chapter 6: Methodology

6.1 Sampling location and programme

Air quality samples were collected from Environment Canterbury's Coles Place monitoring site during 2001 and 2002. This site was selected, as it is the primary residential monitoring site for Christchurch. Measurements from this residential location are evaluated against guideline and NES values, are used to establish long-term trends in air quality, and to develop air quality strategies for managing air quality in Christchurch. In addition, meteorological and other air quality parameters routinely measured at the site were available to provide supplementary information of value to the study.

Monitoring was conducted during summer from November 2001 to March 2002, and in winter from May to August 2002. PM_{2.5} samples were collected on a 24-hour basis from 9 am to 9 am. Unfortunately, during the winter months high particulate loads restricted sample flows resulting in filter blockages. Several high pollution days were invalidated because of these issues. As a mitigation measure, sampling periods were split into two shorter 12-hour periods. These were later aggregated into 24-hour average samples.

Additional sampling was conducted over a three-week period to provide ambient elemental source profiles. These profiles assisted with source identification of the factors resolved by the PMF receptor model. Ambient samples, rather than direct source samples, were collected to allow for chemical transformation from source to receptor. Sites dominated by specific sources were selected, and sampling conducted at times when emissions from other sources were unlikely to contribute. Roadside samples were collected at Riccarton Road and Colombo Street from Tuesday to Friday during the hours of 8 am to 12 pm. These provided elemental source profiles for motor vehicles. Residential heating source profiles, conversely, were obtained by sampling air quality in residential backyards in the suburbs of Mairehau (Thornton Street) and Aranui (Sandown Crescent). Samples were collected from Monday to Thursday during the hours of 8 pm to 12 am.

6.1.1 Site descriptions

Figure 6.1 shows the location of the primary "residential" monitoring site (Coles Place), and the "motor vehicle" sites at Riccarton Road (Riccarton), Colombo Street (City), and "residential heating" sites at Sandown Crescent (Aranui) and Thornton Street (Mairehau).

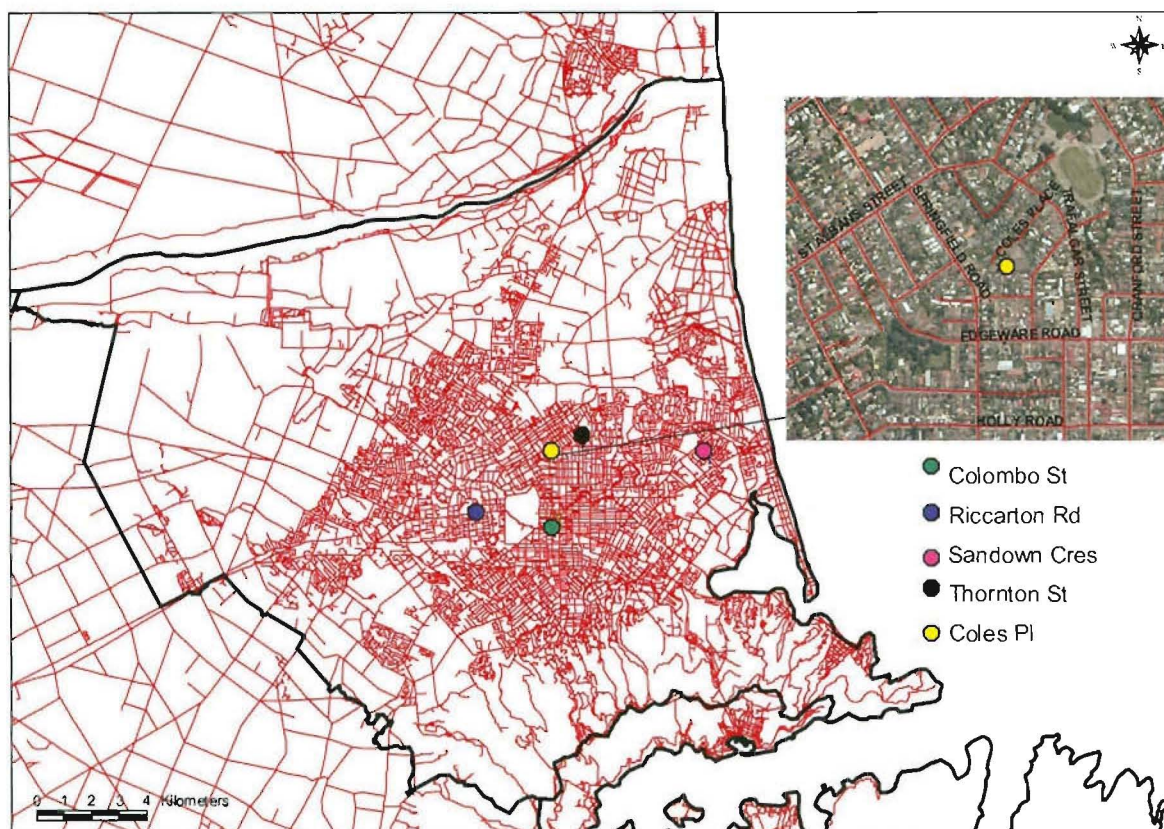


Figure 6.1 Location of the Coles Place monitoring site and the ambient source sites, Christchurch, 2001/2002.

The Coles Place monitoring site is situated in the suburb of St Albans at the end of a quiet cul-de-sac, on a grassed area next to a tennis court and behind a set of residential flats. With the exception of the immediately adjacent land uses, the surrounding built environment (zoned Inner Suburban in the proposed Christchurch City Plan) is dominated by older, medium to high-density residential dwellings. The closest arterial road to the site, Cranford St (State Highway 74), is located approximately 375 m to the east, and Edgeware Road, a busy urban route, is about 240 m to the south. All other roads in close proximity to the site comprise relatively quiet urban streets. Within a 1.5 km radius of the site, there are 16 industrial/commercial activities consented to discharge contaminants to air (Figure 6.2). These are located to the south and west, and consist of a variety of small to medium size boilers and generators (predominantly fuelled by diesel oil or liquid-petroleum gas (LPG)). Closer to the site, there is a 250 kilowatt (kW) diesel fired boiler (350 m to the northeast), two 250 kW diesel fired boilers (500 m to the southeast), and a wood processing industry (450 m to the southeast). Sources outside the 1.5 km radius that may potentially impact on the Coles Place site under certain meteorological conditions, include a number of small to medium size industries located to the south. In particular, two large coal-fired boilers currently operate at the Christchurch Public Hospital and New Zealand Breweries. Other major industries less likely to impact on measured concentrations, include those within the Woolston industrial area (5.5 km to the southeast), some medium sized

sources between 3.5 and 8 km southwest of the site, the Hornby industrial area (7.5 to 10 km southwest), and the Belfast meat works (6.5 km to the north). Potential natural sources of PM_{2.5} in Christchurch include the coastal area, with the closest beach located at New Brighton (approximately 8 km to the east), and rural farmland (mainly market gardens and orchards) located approximately 4 km to the north.

As measurements conducted at Riccarton Road, Colombo Street, Sandown Crescent and Thornton Street were only used to assist with the identification of the source factors, full site descriptions are not provided. The samplers were positioned so that the majority of contaminants measured were from the target source of concern. The "motor vehicle" samples were collected on two of Christchurch's most congested streets, some distance from residential chimneys, and the samplers located directly above the road (three to four metres above ground level). The "residential heating" samples were collected in two residential suburbs of Christchurch, where solid fuel burner use is highly concentrated (based on census information from Statistics New Zealand). The sites were located within the centre of residential areas and a good distance from major roads. Sampling was conducted in residential backyards and the instruments located at ground level. The timing of the sampling was designed to ensure that emissions were primarily from the target source (see previous section).

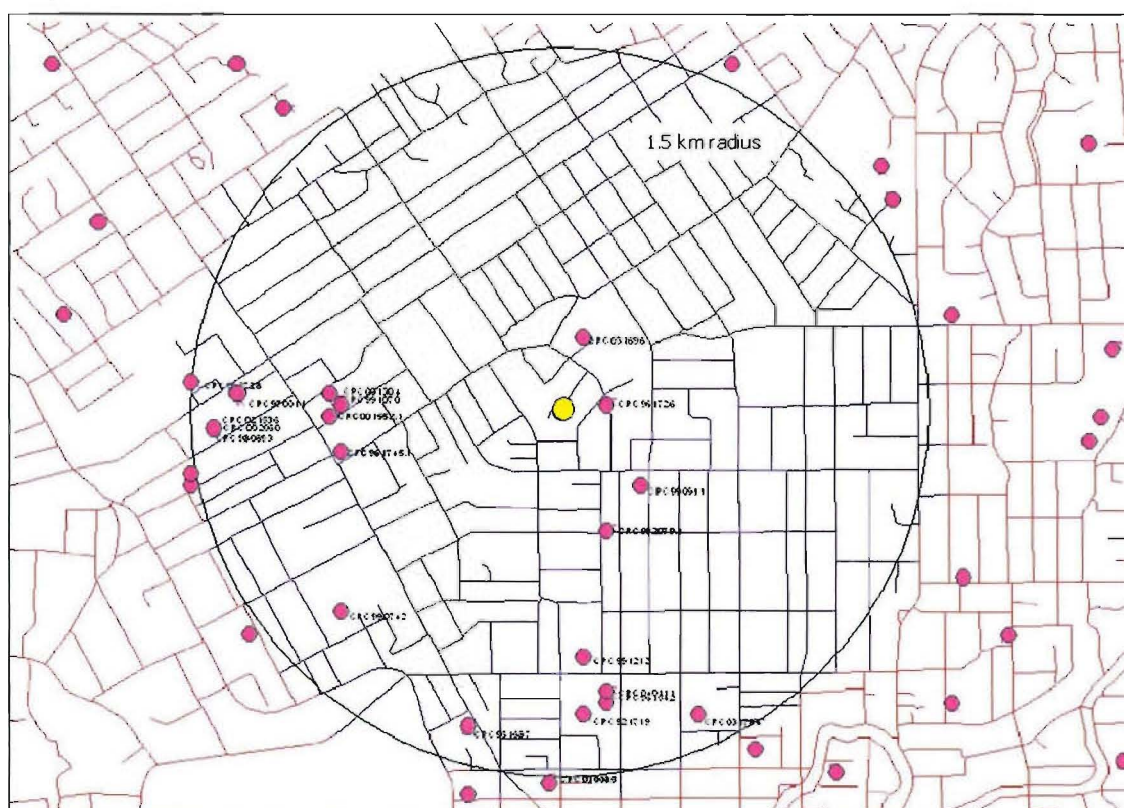


Figure 6.2 Consented industrial/commercial discharges within a 1.5 km radius of Coles Place, Christchurch. Monitoring site location indicated in yellow at centre, and consented activities in pink and by consent number (courtesy of Environment Canterbury).

6.2 Instrumentation and analytical methods

6.2.1 Overview

Table 6.1 provides details of the instrumentation, filter media (where applicable) and analytical techniques employed during this study.

Table 6.1 Summary of instrumentation and methods used for collecting and analysing PM_{2.5}, Christchurch, 2001/2002.

Analyte	Instrument	Filter media	Analytical technique
Fine particles (PM _{2.5})	SuperSASS	Polycarbonate	Gravimetric
Chemical elements (Na, Mg, Al, Si, P, S, Cl, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Br, Rb, Sr, Y, Zr, Ba, Hg and Pb)	SuperSASS MiniVol	Polycarbonate	Proton induced x-ray emission (PIXE)
Inorganic ions (NO ₃ ⁻ , SO ₄ ²⁻ , NH ₄ ⁺ and Cl ⁻)	SuperSASS	Nylon, Teflon	Ion chromatography (IC)
Black carbon	SuperSASS	Polycarbonate	Light reflectance
Elemental and organic carbon (EC and OC)	Series 5400 ambient carbon particulate monitor	N/A	Thermal CO ₂ analysis with an OC/EC differentiation temperature of 230°C

6.2.2 Instrumentation

The primary instrument used in the study was the Speciation Aerosol Sampling System, otherwise known as the SuperSASS. The SuperSASS, a sequential filter-based sampler, collected 24-hour average PM_{2.5} samples for elemental and ionic analysis. The instrument, pictured in Figure 6.3, consisted of a tripod, control box, vacuum pump, eight sampling canisters and a solar shield. A schematic of the instrument is also provided (Figure 6.4).

Individual canisters, located under the solar shield, are fitted with PM_{2.5} sharp cutoff cyclone (SCC) inlets and tandem filter holders. Ambient air is drawn through each canister and transmitted cyclonically through the SCC. Inertia created by the cyclone removes particles greater than 2.5 µm, with the remaining particles collected on filters contained in the canister.

Two canisters with varying configurations were used to sample different target analytes. The first canister contained a 47 mm diameter, 0.4 µm³⁰ pore size polycarbonate filter to collect PM_{2.5} mass for gravimetric analysis and trace element determination (elements ranging from sodium to lead). These filters were transported to GNS for elemental analysis by the PIXE technique. BC (EC) was also determined by GNS using a light reflection/transmission technique.

³⁰ During the winter months, filters with different pore sizes were trialled to determine whether pore size contributed to the filter blockage issues. Both 1 µm and 2 µm polycarbonate filters were used, but as these did not resolve the filter blockage issue, the study continued using 0.4 µm filters.

The second canister contained a magnesium oxide denuder to remove gaseous nitrogen species, a 47 mm diameter, 0.5 μm pore size teflon filter and a 0.45 μm pore size nylon filter to collect particulate for inorganic ion analysis (nitrates, sulphates, chloride and ammonium). These filters were transferred to the Environment Canterbury laboratory and analysed using the IC technique.



Figure 6.3 Changing the SuperSASS canisters at Coles Place (starring Mark Harvey, Environment Canterbury).

EC and OC were measured on a continuous basis using a Rupprecht & Patashnick (R&P) Series 5400 ambient carbon particulate monitor. Measurements were conducted hourly and averaged over 24 hours to obtain daily data. A thermal CO_2 analytical technique was used by the instrument to differentiate between OC and EC.

The ambient source samples were collected using MiniVol portable air samplers. MiniVols draw low volumes of ambient air (5 l min^{-1}) through an impactor to collect particulate matter on a filter. The impactor restricts particle collection to the $\text{PM}_{2.5}$ size fraction. The impactor grease used in the MiniVol samplers was Apiezon rather than the standard silicon-based product, which is not suitable for speciation studies.³¹

³¹ Apiezon grease does not interfere with the measured sample or the subsequent elemental analysis.

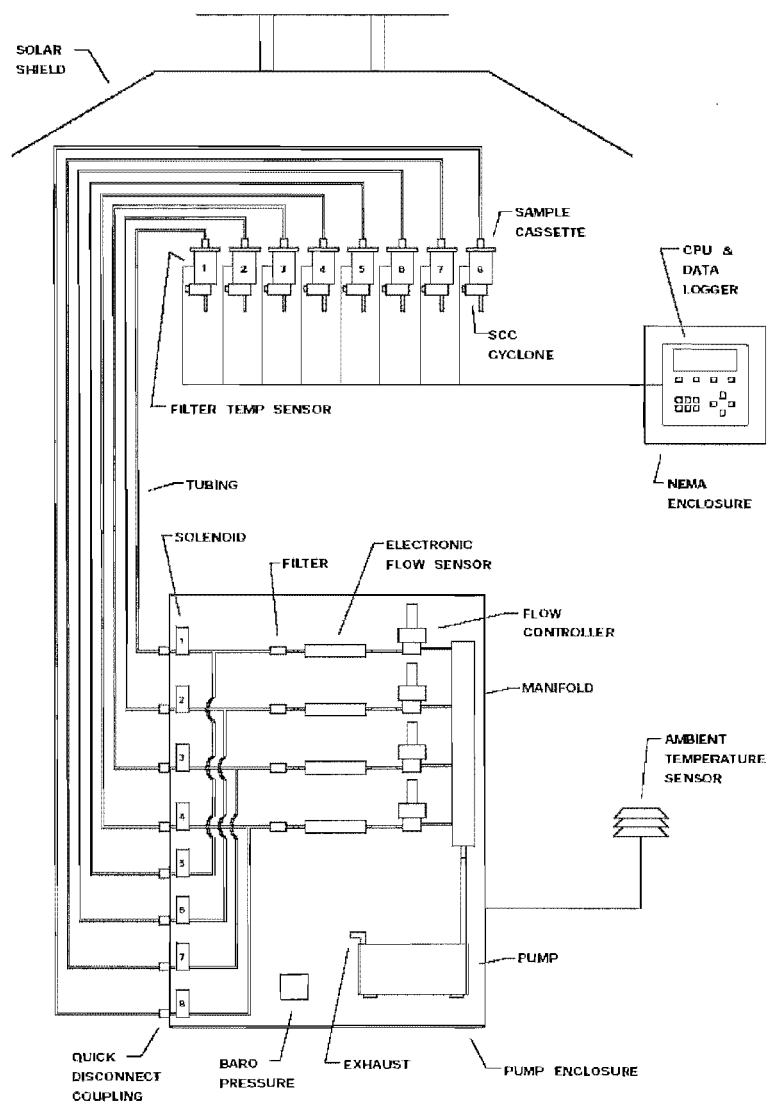


Figure 6.4 Flow diagram for the SuperSASS (courtesy of Met One Instruments).

6.2.3 Filter media

The selection of appropriate filter media is critical in the collection of PM for speciation. In particular, consideration must be given to filter compatibility with the analytical methods and analytes selected for study, particle collection efficiencies, pressure drop issues, and cost.

A review of the applicable literature, and studies conducted in New Zealand, led to the selection of polycarbonate filters for the gravimetric and elemental analysis, and tandem nylon/teflon filters for the inorganic ions (Lee and Makund, 2001; University of California, 1995; Watson and Chow, 2001; Chow and Watson, 1998; Met One, 2001; Wilton, 2003; Davy, 2002a,b).

Polycarbonate filters (Nuclepore) were selected for analysis by PIXE, in preference to Teflon.³² These filters comprise a thin polycarbonate membrane with uniform sized pores located across the membrane surface. However, the study revealed that polycarbonate filters were prone to blockages under high particulate loading conditions (e.g. during the winter months). Meteorological parameters such as humidity, and the tar-like nature of wood burning particles were the most likely factors contributing to these blockages. Subsequent investigation has found that Teflon filters may be more suitable media for wintertime use, as they are able to withstand higher particle loadings before restricting flows. Thin ringed Teflon filters have been used and analysed successfully by PIXE in studies conducted elsewhere (Perry Davy, Greater Wellington, *pers. comm.*).

The selection of filters for the measurement of inorganic ions is slightly more complicated owing to artifact formation issues. The literature suggests nylon filters are suitable for the collection of nitrates as HNO_3 formed from the vaporisation of particulate nitrate is passively adsorbed onto the surface of the filter (Met One, 2001; Watson and Chow, 2001). However, these filters are not suitable for sulphate analysis, as SO_2 is adsorbed onto the filter surface. Teflon filters are not subject to sulphate artifact formation, but are prone to nitrate loss (in the form of NH_4NO_3 and HNO_3). Consequently, the most suitable sampling system consists of a denuder (to eliminate gas phase HNO_3), and filters in tandem with a primary Teflon filter (for ammonium, chloride and sulphates) followed by a nylon filter (for nitrates). This configuration was adopted for the source apportionment study. Unfortunately, cost considerations led to the extraction of both nylon and Teflon filters in the same solution, which offset the benefits of the dual filter system. Although this places a greater degree of uncertainty on the sulphate results, it is unlikely to be highly significant.³³

6.2.4 Analytical methods

Gravimetric analysis

Gravimetric analysis involves the measurement of net particulate mass collected on a filter. The filter is weighed prior to and following sampling in a temperature and humidity-controlled environment. Filters are conditioned over a 24-hour period to minimise particulate volatilisation and moisture bias, and weighing is conducted using a micro-balance with sufficient sensitivity (Chow and Watson, 1998).

During the study, the polycarbonate filters were conditioned in a dessicator for a 24-hour period prior to pre-weighing. The dessicant material used was potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) and the filter was maintained at a relative humidity of approximately 60%. The filters were weighed using a Mettler micro-balance and the weight recorded on the field sheet (Appendix 1). After sampling was completed, the canisters were dismantled and the polycarbonate filters conditioned for another 24-

³² Fluorine present in Teflon filters interacts with the proton beam used in PIXE. This creates a γ -ray background which interferes with the analysis (Dzubay and Stevens, 1991).

³³ Nevertheless, the sulphate measurements were excluded from the source apportionment analysis because of this issue.

hours. The filters were re-weighed and the weights recorded on the field sheet. The difference between initial gravimetric weight and the final weight constituted the $PM_{2.5}$ mass measurement. These values were transformed into concentrations using the methodology described in Appendix 2.

Proton induced x-ray emission (PIXE)

Subsequent to determining particulate gravimetric mass, the samples were transferred to GNS for elemental analysis. PIXE, a non-destructive, multi-elemental technique, was used to identify the elemental composition of each sample. A 15 mm diameter proton beam, accelerated with 2.5 million volts from a van-de-Graff accelerator, was used to bombard the sample with protons (Figure 6.5; Trompetter and Markwitz, 2002). Each elemental atom present in the sample ejects inner shell electrons which then release characteristic fluorescent x-ray photons (Chow and Watson, 1998). The x-rays allow each element to be identified and for concentrations to be determined. Two detectors were used to measure x-rays from the light and heavy elements. Complex spectra with overlapping peaks were generated and deconvolved using Gupix Software (Figure 6.5), and data provided in $ng\ cm^{-2}$ units. The method for converting data into concentrations is outlined in Appendix 2. Additional detail regarding the PIXE analysis may be found in Trompetter and Markwitz (2002).

Light reflectance

The polycarbonate filters transported to GNS for analysis, were also analysed for BC (EC) using a M43D digital smoke stain reflectometer. A light is transmitted through the sample onto a photocell and the amount of light absorbed is directly attributed to EC. This is based on the premise that EC is the most highly absorbing chemical compound present in particulate matter (Horvath, 1993). The results are provided in $ng\ cm^{-2}$ and converted into concentrations using the methodology outlined in Appendix 2.

Ion chromatography (IC)

IC is a common technique used to measure water-soluble (or inorganic) ions in PM. The water-soluble component of $PM_{2.5}$ is extracted from each sample using de-ionised water. The sample is injected into an eluent that passes through an ion exchange column. The ions are separated by the column, which uses a conductivity detector to quantify individual species. After passing through the ion exchange column, the sample enters a suppressor column where the chemical composition of one element is altered, producing a matrix of low conductivity. The ions are identified by the retention time and quantified by the conductivity peak area (Chow and Watson, 1998).

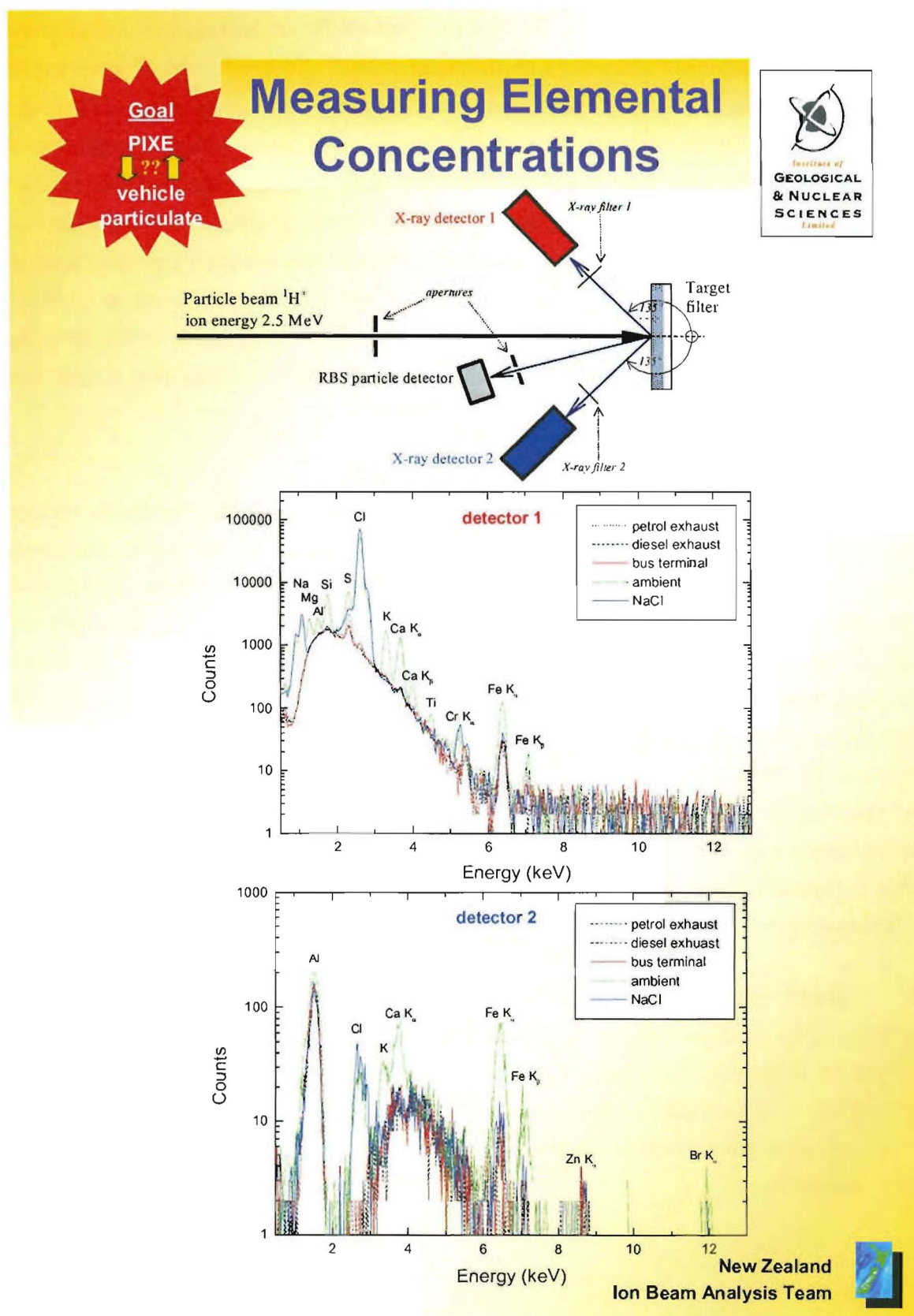


Figure 6.5

Schematic diagram depicting measurement by PIXE (top) and the spectra used to determine concentrations (centre and bottom; courtesy of the Institute of Geological and Nuclear Sciences).

During the study, the nylon and teflon filters used to collect PM for ion analysis were collected and placed into a single, small vial with 20 ml of de-ionised water.³⁴ To ensure that all water-soluble material was extracted, the samples were aged in a refrigerator. An extract of 50 μl from each sample was injected into the sodium carbonate/bicarbonate eluent, which passed through the ion exchange column. Fluorides were measured separately using a Borax eluent. A Dionex CD20 conductivity detector measured the concentrations of the individual species. Ammonium was measured by a continuous flow analyser using a phenate method. The analytical laboratory provided results for chloride, nitrate nitrogen, sulphate, fluoride and ammonia nitrogen in units of $\mu\text{g filter}^{-1}$. Conversion of the data into concentrations is detailed in Appendix 2. Investigation of the nylon filter blanks revealed high background levels of chloride. The chloride concentrations were subsequently eliminated from the dataset.

Thermal CO₂ analysis

The principle employed by the R&P Series 5400 ambient carbon particulate monitor to measure carbon is similar to the thermal optical reflectance/transmission method used elsewhere. The sample is heated, oxidised at elevated temperatures and measured using a nondisperse infrared (NDIR) CO₂ detector (Chow and Watson, 1998; Wilton, 2003). Differentiation between OC and EC is operationally defined and determined by the temperature settings of the instrument. In this instance, the amount of CO₂ released when the sample was combusted at 230°C was attributed to OC. Similarly, CO₂ produced at a combustion temperature of 750°C (with the 230°C measurement subtracted) was attributed to EC (Wilton, 2003). As OC is oxidised during analysis, the measurement provided in $\mu\text{g m}^{-3}$ does not reflect total organic mass (Seinfeld and Pandis, 1998). The OC value, representing carbon molecules only, must be converted to a mass equivalent. Data transformation details are included in Appendix 2. Results obtained by this method should only be compared with studies using a similar analytical technique.

6.3 Data transformation and validation

Table 6.2 outlines field and analytical data collected during the study for validation and data transformation purposes. Data were not always provided in the required form or units and transformations were necessary to calculate concentrations in $\mu\text{g m}^{-3}$. Validated and transformed data were compiled into a matrix of elemental concentrations (as denoted by *m*) and by observation (or date, denoted by *n*).

³⁴ The teflon and nylon filters were placed into the same vial to reduce the analytical costs. It has since been realised that this was an error and may have compromised the accuracy of the sulphate concentrations.

Table 6.2 Field and analytical data summary.

Field data parameters	Analytical data characteristics
<ul style="list-style-type: none"> Start date Event length (hours) Ambient pressure (mmHg) Ambient temperature (°C) Filter temperature (°C) Mean flow (l min⁻¹) Total volume (m³) Max dT (indicates temperature incursions) Temperature warnings Flow warnings Power interruptions 	Gravimetric PM _{2.5} mass (g) <ul style="list-style-type: none"> Start weight End weight Weight difference 24-hour samples in summer 2 x 12-hour samples in winter Elements (ng cm ⁻²) <ul style="list-style-type: none"> 24-hour samples in summer 2 x 12-hour samples in winter Inorganic ions (µg filter ⁻¹) <ul style="list-style-type: none"> 24-hour samples in summer 2 x 12-hour samples in winter BC (ng cm ⁻²) <ul style="list-style-type: none"> 24-hour samples in summer 2 x 12-hour samples in winter EC and OC (µg m ⁻³) – hourly data

6.3.1 Data transformation

Transformations required were:

- the aggregation of 12-hour field and concentration data into 24-hour average values
- conversion of data from ng cm⁻² to µg m⁻³
- standardisation of air quality measurements by air pressure and temperature
- conversion of ammonia nitrogen to ammonium, and nitrate nitrogen to nitrate
- adjustment of OC to account for other elemental species present in organic compounds.

In addition, PMF receptor modelling required the compilation of a concentration and error (or uncertainty) matrix of elemental concentrations by observation. Both matrices were required to be complete, with no missing data. The method of substituting missing data with estimated values, and for allocating errors to each concentration value was based on the approach suggested by Polissar *et al.* (1998). Progressively higher uncertainties were allocated to below detection limit, zero and missing data. Appendix 2 details the transformations for each data type, data substitution methods for missing data, and methods used to allocate uncertainties to zero, below detection limit and missing data.

6.3.2 Data validation

Data in the transformed concentration matrix (x_{ij}) were scrutinised for errors and validation procedures applied. Field and instrumental records provided by the SuperSASS highlighted sampling errors, such as invalid flow rates (<6.03 and >7.37 l min⁻¹) and sampling times (<23 and >25 hours), and included notes from field and lab staff regarding suspect samples. A total of 20 sampling days were invalidated for reasons ranging from inadequate flows and sampling times to negative mass balances. There were 17 days when the PM₁₀ guideline of 50 µg m⁻³ was exceeded during the winter of 2002. Unfortunately, speciated measurements could only be collected for six of these days due to the filter overloading issues. Table 6.3 lists sampling days removed from the dataset and provides the basis for invalidation.

Table 6.3 Invalidated sampling days, Christchurch, 2001/2002.

Invalidated days	Basis for invalidation
3 December 2001	Power cut
25 January 2002	Filter blockage
11 February 2002	Instrument problems
13 February 2002	Instrument problems
14 February 2002	Instrument problems
15 February 2002	Instrument problems
18 February 2002	Instrument problems
21 February 2002	Insufficient sample time
11 March 2002	Negative mass balance value
26 March 2002	Power interruptions
8 May 2002	Power interruptions
1 June 2002	Filter overloaded, insufficient flow
2 June 2002	Filter overloaded, insufficient flow
4 June 2002	Filter overloaded, insufficient flow
10 June 2002	Filter overloaded, insufficient flow
25 June 2002	Filter overloaded, insufficient flow
2 July 2002	Filter overloaded, insufficient flow
3 July 2002	Filter overloaded, insufficient flow
17 July 2002	Filter overloaded, insufficient flow
19 July 2002	Filter overloaded, insufficient flow

The percentages of observations greater than zero and above limits of detection were used to determine which elemental and ionic species to include in the receptor modelling. These are outlined in Table 6.4. Chemical species with less than 70% of data above zero were excluded from further assessment. These included phosphorus, scandium, titanium, vanadium, manganese, cobalt, copper, gallium, germanium, arsenic, selenium, bromine, rubidium, strontium, yttrium, zirconium, barium, mercury, lead and fluoride.

The remaining valid data were graphed into time series and scatter plots to determine whether any anomalies were present in the data. Several species had questionable data points including sodium, aluminium, silicon, chlorine, nickel and iron. Comparisons with other elemental species demonstrated similar concentration patterns suggesting that the values were valid. Aluminium, silicon and nitrate

had single suspicious data points that contrasted with those of other species. The values were checked with the analytical laboratories and were confirmed as correct. A robust reason could not be found to invalidate these data so the values remained in the dataset. However, errors for the suspect data points were increased to reduce the influence of these data on the receptor model output.

Table 6.4 Percentage of days greater than zero and above limits of detection, Christchurch, 2001/2002.

Element	% >LOD	% <LOD	% Zero data	Total % non-zero data
BC	84	7	9	91
Na	79	15	6	94
Mg	91	8	1	99
Al	19	53	27	73
Si	100	0	0	100
P	6	35	59	41
S	100	0	0	100
Cl	100	0	0	100
K	93	7	0	100
Ca	72	23	4	96
Sc	4	46	50	50
Ti	6	46	48	52
V	6	34	59	41
Cr	41	55	4	96
Mn	8	45	47	53
Fe	100	0	0	100
Co	2	38	60	40
Ni	29	54	16	84
Cu	14	45	41	59
Zn	67	23	10	90
Ga	1	22	77	23
Ge	2	26	72	28
As	22	30	48	52
Se	0	16	84	16
Br	13	46	42	58
Rb	0	17	83	17
Sr	0	16	84	16
Y	0	14	86	14
Zr	0	11	89	11
Ba	1	35	65	35
Hg	0	24	76	24
Pb	7	46	47	53
NH ₄ ⁺	86			86
NO ₃ ⁻	71			71
SO ₄ ²⁻	93			93
OC	100			100
EC	100			100

The EC and OC data were quality assured using the standard validation procedures employed by Environment Canterbury.³⁵ The data were entered into the spreadsheet and OC converted to organic mass (OC_{mass}) as indicated in Appendix 2. The MiniVol data were not converted into elemental concentrations. The data were only required for factor identification purposes, and as such, relative elemental abundances (in percentages) were sufficient.

6.4 Analysis and presentation of speciated data

Prior to conducting receptor modelling by PMF, a statistical analysis of the valid dataset was undertaken using Statistica 6.0. Data excluded from the modelling were chemical species with less than 70% of data above zero, sulphate and EC. The latter elements were excluded to prevent double-counting with the sulphur and BC measurements, and because of the potential uncertainty associated with the sulphate measurements.

The statistical analysis describes distributions of chemical species and identifies relationships between variables. Typically, air quality data are not normally distributed due to fluctuations in meteorological conditions and contaminant emissions. Non-parametric techniques were therefore selected to characterise the speciated dataset.

Basic statistics were compiled, including those listed in Table 6.5. Measures of location and dispersion, such as these, provide a useful overview of the distribution of the speciated data.

Table 6.5 Descriptive statistics used in the study.

Measure	Description
Mean	The central tendency of a variable.
Median	The middle value, 50% of cases fall below the median and 50% above. This value can indicate skewness if substantially different from the mean.
Minimum	The smallest value.
Maximum	The largest value.
25 th percentile	The 25 th percentile represents the value at which 25% of the data fall below that value. It is also referred to as the .25 quantile or lower quartile.
75 th percentile	The 75 th percentile represents that value at which 75% of the data fall below that value. It is also referred to as the .75 quantile or upper quartile.
Standard deviation	This is the positive square root of variance.

Sources: Davis (1973), Kim and Mueller (1978), McBride *et al.* (1999), Statistica Electronic Manual

Box and whisker plots provide a visual representation of the data distribution. The plots identify the central tendency of each variable (a marker represents the median), the variability of the data (a box represents the 25th and 75th percentiles), and the minimum and maximum values (as represented by the whiskers). Outliers and extremes are also presented and include those values that are "far" from the middle of the distribution. For a definition of these refer to the Statistica Electronic Manual (an outlier coefficient of 1.5 was used). The correlation coefficient (r) determines the extent to which the

³⁵ Environment Canterbury's QA procedures are outlined in the manual available at: www.ecan.govt.nz/Air/Airquality/Contents/EMQAirFrontpages.htm.

values of two variables are “proportional” to each other (i.e. the extent to which the variables vary together). The coefficient of determination (r^2) indicates the proportion of common variation in the two variables (i.e. the “strength” or “magnitude” of the relationship between them). To evaluate the correlation it is important to know the magnitude or strength, as well as the significance of the correlation. The statistical significance, otherwise known as the p-level, is the degree to which a result is “true” for a given population. The smaller the p-level, the less likely the relationship between variables is representative of the broader population (i.e. the more unusual it is). So a p-level of 0.05 (0.01) indicates that there is a 5% (1%) probability that the relationship between two variables occurred by chance. The p-level therefore represents the probability of error that is involved in accepting the relationship as a statistically significant one.

To determine the relationship between chemical species, Spearman Rank (Spearman R) correlation coefficients were computed. Spearman R is similar to the more commonly used Pearson product-moment correlation coefficient in terms of the proportion of variability accounted for. The difference is that Spearman R measures the strength of the monotonic relationship between sets of ranked data rather than linear relationships between actual values. It is a non-parametric measure and is not as powerful as Pearson product-moment correlation in being able to evaluate correlations between variables. If variables are related the correlation coefficient will lie close to 1 or -1 . Values close to zero indicate that the variables are independent and a relationship does not exist. Although analyses were conducted separately for the summer and winter datasets, only relationships obtained from the combined dataset are actually presented. Variables with coefficients >0.7 and significant at $p < 0.05$ are highlighted in the coefficient matrix. A visual presentation of the relationships between variables is also provided in the form of scatter plots and histograms (frequency distributions).

6.5 Receptor modelling

Following review of the available source apportionment literature, PMF was selected as the preferred receptor model for investigation (Section 4.2). However, prior to applying the PMF receptor model, a PCA of the dataset was undertaken. This provided a quick overall assessment of the data, and indicated the potential number of factors and types of elemental profiles that may be derived.

6.5.1 Principal components analysis

PCA was performed on the combined summer and winter data using Statistica 6.0. An 8-factor solution was specified as the starting point for the analysis. Rotation of the data was required to optimise the solution and a varimax raw rotation was conducted.³⁶ Following this step, the eigenvalue screeplot was reviewed to determine whether the appropriate number of factors had been selected (Figure 6.6). The number of factors with an eigenvalue greater than one, or the point at which there is very little variation between factors (each eigenvalue represents a factor), is indicative

³⁶ The rotation maximises the variances of the squared raw loadings across variables for each factor.

of the correct number of factors to select. On this basis, it appeared that four to eight factors were appropriate.

Multiple runs were conducted, and following evaluation of the factor loadings matrices, a five-factor solution was selected. A matrix of factor loadings was generated with each factor representing an elemental source profile, and the loadings, the degree of correlation between the elemental species and the factor. Values with factor loadings greater than 0.7 were considered significant and used to identify potential sources. The results of the PCA are presented in Section 7.7.

While a PCA of the speciated dataset is useful as an initial assessment, it normalises the elemental concentrations thus limiting its ability to conduct a source apportionment of the PM. Also, the factor scores, which are also normalised, cannot be used to determine relative source contributions to total concentrations. Additional methods, or an alternative receptor modelling technique such as PMF, are required to complete the analysis.

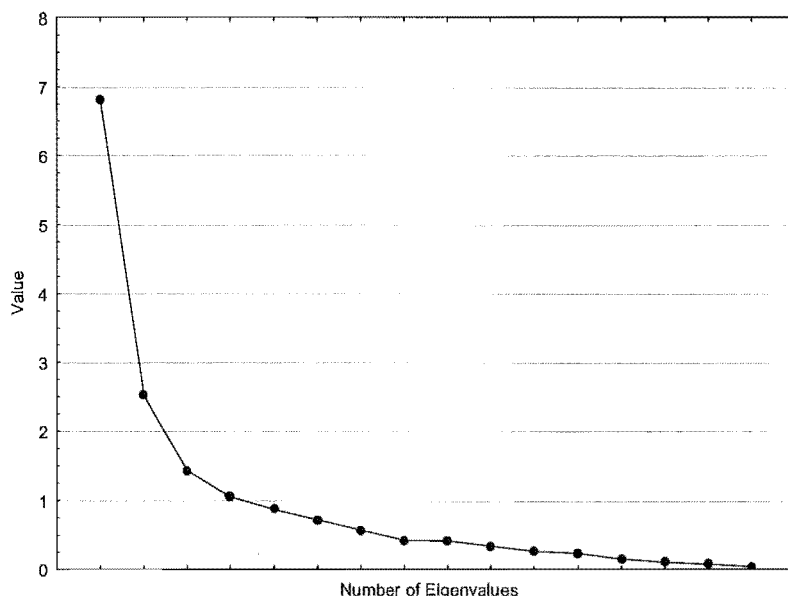


Figure 6.6 Screeplot of eigenvalues derived from the combined summer and winter dataset, Christchurch, 2001/2002.

6.5.2 Positive matrix factorisation

The PMF2 receptor model was applied to the combined summer and wintertime dataset. A preliminary analysis was conducted using 16 chemical species. This was subsequently revised using 15 species following a specific investigation of OC and EC in Christchurch in 2004 (Chapter 8).

The PMF2 modelling software includes an initialisation file, which controls and operates the model. Adjustments are made to this file to define the parameters under which the model operates and the type of information generated. The parameters adjusted to conduct the preliminary source apportionment of the Christchurch data are summarised in Table 6.6 (Chapter 9 for details of the final

analysis). Major data inputs were the concentration and error matrices, compiled in accordance with Appendix 2.

The selection of appropriate values was determined by review of the published literature and by conducting multiple PMF runs. After each run, the model generated a log file, F-Factor matrix, G-Factor matrix and a miscellaneous file (which included a matrix of residuals scaled by the standard deviations). The log file was checked to determine whether convergence³⁷ was achieved (especially at the final stage), the number of residuals exceeding specified outlier threshold distances, presence of any error messages and, most importantly, whether the computed goodness of model fit value, Q, was reasonable.

Table 6.6 PMF modelling parameters, Christchurch, 2001/2002.

Parameter	Adjustments
Title line	This is a text line that is used to provide details regarding the dataset and any exclusions.
Dimensions	This specifies the number of rows, columns, factors and repeats required. The Christchurch dataset used was a matrix with 159 rows and 16 columns. Five factors were selected based on the results of multiple runs and the PCA analysis. Twenty repeats were initially selected to ensure that a solution based on the true "minimum" sum of squares value was used.
F-peak	Controls the rotations. When a positive value is set, G vectors are added together and the corresponding F factors are subtracted from each other (Hopke, undated). The f-peak value that obtained the best solution was 0.
Mode	Determines how the model deals with outliers. The "robust" mode was selected as this is most appropriate for environmental data with true outliers. A threshold outlier-distance of 4.0 was allocated.
Code C3 and error model	These work together with other codes and arrays to determine how the program reads and/or computes error values. Following the recommendation of Paatero (2000a,b), the EM-14 model was used due to its suitability for general-purpose environmental work. Code C3 refers to the element of relative error that exists. A value of 5% was used. Codes C1 and C2 did not need to be adjusted as an uncertainty matrix was provided.
Lims and Chi-2 test	The program runs in three stages with different limit repulsion values "lims". These may be adjusted so that convergence is achieved quickly. The lim values selected were 1.0, 0.3 and 0.003. The Chi-2 test is used to test whether the iteration has converged to a true local minimum. Values of 0.5, 0.1 and 0.01 were used.
Line 30 & 31	These indicate to the programme the location and names of the input files. The first is the concentration matrix and the second is the error matrix.

Source: Hopke (undated); Paatero (2000a,b).

Priority during the initial stage of the analysis was given to obtaining an acceptable Q-value. The computed Q or Chi-2 value may be used to optimise the number of factors and, if there are no outliers and the error modelling is correct, should approximately equal the number of data points in the concentration matrix (Paatero, 2000b). The theoretical Q-value for the Christchurch 159 x 16 dataset, on this basis, was 2544. However, personal communication with Phil Hopke (Clarkson University, Potsdam, USA) indicated that the theoretical Q value is defined as:

³⁷ Convergence is a concept related to iterative computations, where each new set of values (e.g. the values of F and G) is computed based on the previous set. There should eventually be very little change from the old to the new set of values so that the sequence comes to a halt. This is referred to as convergence. In other words, convergence means that the iteration has reached F and G values where Q cannot be decreased any further by adjustment of F and/or G (Pentti Paatero, University of Helsinki, Finland, *pers. comm.*).

$$Q = n * m - p * (n + m) \quad [23]$$

where: n is the number of samples, m is the number of chemical species and p the number of factors selected.

On this basis, the theoretical Q would be 1669. As it is uncertain which rule applies, the theoretical Q value for the preliminary analysis is assumed to be between 1669 and 2554. Q -values, obtained by each PMF modelling run, were evaluated against this estimated value. It became evident during this process that error values for some chemical species in the Christchurch dataset (e.g. ammonium, nitrate and sodium) were inappropriately allocated. These were adjusted as detailed in Appendix 2.

Subsequent to obtaining Q -values within an acceptable range, the corresponding F-Factor matrices were reviewed to determine whether the resolved factors made physical sense. The F-Factor matrices output from the model detailed elemental loadings for each factor. Elemental source profiles were obtained directly from the F-Factor matrix by calculating the relative elemental contributions to total source mass.

Continual evaluation of the residuals, source profiles and calculated Q values assisted in determining the appropriate number of factors, and the optimum f-peak, error model and lim values to use. Further consideration was given to the regression coefficients derived when the G-Factor matrix, comprising factor scores for each sampling day, was regressed against gravimetric $PM_{2.5}$ mass. Negative regression coefficients can be indicative of unrealistic factor number selection (Ramadan *et al.*, 2000). The G-Factor matrix derived from the final five-factor solution was exported into Statistica 6.0. Multiple Linear Regression (MLR) was conducted by selecting $PM_{2.5}$ as the dependent variable and the factor scores as the independent variables. The constant of the regression was assumed to be zero (by setting the intercept to zero). Positive coefficients were calculated and included Beta (produced by standardising all variables to a mean of zero and a standard deviation of 1) and B (these are the raw unstandardised coefficients). The B coefficients were multiplied by the factor scores (G-Factor matrix) to calculate daily source contributions.

During the analytical stage of the study, it became evident that there were some issues associated with the OC data used in the receptor modelling. An additional investigation of these chemical species was conducted (Chapter 8), the dataset revised and reanalysed by PMF. The final source apportionment results for this study are presented in Chapter 9 and include:

- average contributions from each source to average PMF mass, calculated on a monthly and seasonal basis (summer (November to March) and winter (May to August))
- contributions from each source to maximum PMF mass for each month and season.

6.6 Evaluation of modelling quality

To evaluate the success of PMF as a source apportionment tool, the quality of the model output is determined. This is conducted in two parts where the accuracy of the source identification is evaluated, and secondly, where the ability of the model to estimate source contributions is examined.

In Chapter 10, the chemical composition of each source profile is evaluated against ambient source samples collected during the study, direct source profiles obtained from New Zealand and overseas, and factors resolved in the literature. The daily source contributions are graphed and reviewed to determine whether sensible seasonal patterns exist. Meteorological and contaminant data for peak source events were also evaluated. Quality of the source identification with regard to chemical composition, seasonality of the source contributions and characteristic nature of the meteorological conditions are discussed. In addition, the morphological characteristics of particles present on the peak contribution days were evaluated, where possible. This was conducted by reviewing micrographs of particles produced by scanning electron microscopy (SEM). Perry Davy of Greater Wellington Regional Council prepared and examined several PM_{2.5} samples collected during this study by SEM. A small 11 mm disc was cut from each filter and placed onto 12.5 mm aluminium stubs with carbon tape. The samples were then coated with a 4 nm layer of gold and the SEM analysis conducted using a JEOL JSM 6500F at Victoria University in Wellington. Particles of interest were selected, micrographs compiled and the elemental composition of each particle determined using Energy Dispersive Spectroscopy (EDS).

In Chapter 11, the ability of the PMF receptor model to quantify contributions to PM_{2.5} is assessed. The matrix of residuals scaled by the standard deviations output by PMF was entered into Statistica 6.0 and frequency distributions obtained. Paatero (2002b) suggested that if the correct number of factors is selected, and the errors allocated appropriately, then the residuals should fall between -2 and 2. The residuals were also useful in the validation of the dataset, as any odd data points were readily identified. The amount of mass accounted for by the elemental species measured, and by the modelling, was also determined by reconstructing PM mass using standard conversion equations (e.g. Brook *et al.*, 1997). The reconstructed mass was plotted against actual gravimetric mass to quantify the proportion of unexplained mass. A similar approach was adopted to assess how much of the mass could be explained by the resolved sources. The sum of the daily source contributions (PMF mass) prior to and after regression, was plotted against measured mass. Separate plots were compiled for the summer and winter datasets to evaluate seasonal differences. Unexplained mass was then graphed against different sources and elemental species to ascertain whether the unexplained component was strongly associated with a particular source type.

The final evaluation method employed was to conduct a "reconciliation" exercise where source contributions were compared using two different techniques. PM_{2.5} data from the 2002 emission

inventory were input into a chemical box model to predict concentrations (refer to Chapter 11 for more details on the methodology used). The box-modelled data, representing the contributions under worst-case wintertime meteorological conditions, were then evaluated against the receptor model results for the maximum $\text{PM}_{2.5}$ day.

6.7 Summary

Speciated air quality data were collected on a 24-hour basis at Environment Canterbury's Coles Place monitoring site. Sampling was conducted using a filter-based SuperSASS, several MiniVols, and a Series 5400 ambient carbon particulate monitor during the summer of 2001/2002 and winter of 2002. Fine particles were determined gravimetrically, elemental species by PIXE, inorganic ions by IC and carbon particulate by Thermal CO_2 Analysis.

Data were validated, transformed and compiled into complete concentration and error matrices with no missing data. A statistical analysis of the data was conducted to determine the range and distribution of chemical concentrations and the relationships between chemical species. The PCA receptor model was applied to the data to gain an initial understanding of potential sources and their chemical profiles. This was followed by a PMF analysis of the total dataset to identify the key sources and their contributions to 24-hour average $\text{PM}_{2.5}$. However, issues associated with the OC and EC measurements led to a separate specific study of OC and EC, and a subsequent revision of the PMF analysis. The OC/EC results are discussed in Chapter 8, and the revised PMF analysis in Chapters 9 and 10. The quality of the modelling was assessed by firstly evaluating the quality of the source profiles and their identification, and the ability of the model to estimate source contributions by investigating the residuals, amount of mass explained by the analysis and by comparing the PMF results with box-modelled emission inventory data. The results of this assessment are discussed in Chapters 10 and 11.

Chapter 7: Results

The results of the study are presented in the following chapters, based on the analysis of the combined summer and winter dataset. Where relevant, the seasonal data are discussed separately. This chapter describes the chemical composition of PM_{2.5} in Christchurch, presents the chemical concentrations, determines the relationship between chemical constituents, and outlines the results of the preliminary PCA and PMF analyses.

These results must be considered in the context of the meteorological conditions prevalent over the course of the study. In brief, the meteorology was variable and not generally conducive to pollutant formation or accumulation. During the summer, conditions were unsettled with cloudier and wetter weather than normal. Winter conditions, also unsettled, were characterised by mild and cloudy weather. Anticyclones moved quickly over Christchurch during that time with fewer cold, calm and clear nights relative to other years. The impact of meteorology on pollutant concentrations was evident, with only 17 exceedences of the PM₁₀ standard (50 µg m⁻³) recorded in 2002. Conversely, in 2001 when the winter season was typified by cold, calm conditions there were 39 exceedences of the standard (Aberkane *et al.*, 2004a,b).

7.1 Distribution of chemical species

The elemental constituents of PM_{2.5} for the summer (November 2001 to March 2002) and winter (May to August 2002) months are presented. Summary statistics in Table 7.1 indicate that OC_{mass}³⁸ BC (an alternative measure of EC), EC, sulphate, sodium, chlorine and sulphur were the most abundant species present in summertime PM_{2.5}. Similar species, along with nitrate, dominated in the winter. The chemical composition of PM_{2.5} in Christchurch is similar to that found in other urban environments where OC, EC, nitrate, sulphate, and ammonium are the major chemical constituents (Tropp *et al.*, 2002; Chow *et al.*, 1993; Chow *et al.*, 1994). The influence of the maritime environment on fine particles in Christchurch is also evident, as indicated by the abundance of sodium and chlorine.

Figure 7.1a and b present the summer and wintertime distribution of EC, BC, OC_{mass} and PM_{2.5} in the form of box-and-whisker plots. The box represents the quartile range (between the 25th and 75th percentiles), the marker denotes the median value and the whiskers the minimum and maximum concentrations. Outliers and extreme values are also indicated.

³⁸ The Series 5400 OC data were multiplied by 1.4 to account for unmeasured elements in the molecular mass of organic compounds. It is a fairly standard aerosol conversion and this, and other equations, may be found at: <http://vista/circa.colostate.edu/improve/Tools/AerTypeEqs.htm>. However, there are issues associated with this conversion and these are discussed in Chapter 8.

Table 7.1 Summary statistics of chemical species present in 24-hour average PM_{2.5} ($\mu\text{g m}^{-3}$), Christchurch, 2001/2002.

SUMMER (November 2001 to March 2002)								
Species	Mean	Valid N	Median	Minimum	Maximum	25th percentile	75th percentile	Standard deviation
S	0.4	65	0.4	0.1	1.3	0.3	0.6	0.2
Cl	0.5	65	0.5	0.03	2.1	0.1	0.7	0.5
Si	0.1	65	0.1	0.05	0.2	0.1	0.1	0.03
Fe	0.03	65	0.03	0.01	0.1	0.02	0.0	0.01
K	0.05	65	0.04	0.01	0.2	0.03	0.1	0.03
Mg	0.1	65	0.1	0.02	0.2	0.1	0.1	0.04
Na	0.8	65	0.8	0	2.0	0.5	1.1	0.4
Ca	0.04	65	0.04	0.003	0.1	0.02	0.05	0.02
Zn	0.01	65	0.01	0	0.1	0.002	0.01	0.01
Cr	0.01	65	0.01	0	0.02	0.003	0.01	0.003
Ni	0.003	65	0.003	0	0.01	0.002	0.004	0.002
Al	0.02	65	0.02	0	0.1	0.002	0.03	0.02
NH ₄ ⁺	0.1	65	0.1	0.01	0.9	0.01	0.2	0.2
NO ₃ ⁻	0.2	65	0.02	0.02	1.3	0.02	0.4	0.3
SO ₄ ²⁻	0.8	65	0.8	0.02	2.3	0.5	1.0	0.4
EC	0.5	65	0.5	0.2	1.7	0.4	0.6	0.3
BC	1.1	65	0.9	0.2	3.4	0.6	1.3	0.6
OC _{mass}	1.0	65	0.9	0.4	2.4	0.7	1.2	0.5
PM _{2.5}	6.4	65	5.5	1.1	28.3	3.4	7.6	5.2
WINTER (May to August 2002)								
Species	Mean	Valid N	Median	Minimum	Maximum	25th percentile	75th percentile	Standard deviation
S	0.5	94	0.5	0.1	1.0	0.4	0.7	0.2
Cl	0.5	94	0.4	0.1	2.5	0.2	0.6	0.4
Si	0.1	94	0.1	0.1	0.3	0.1	0.2	0.04
Fe	0.1	94	0.1	0.02	0.2	0.04	0.1	0.02
K	0.3	94	0.2	0.04	0.9	0.1	0.3	0.2
Mg	0.1	94	0.1	0.04	0.3	0.1	0.2	0.05
Na	0.6	94	0.5	0.01	2.4	0.3	0.7	0.4
Ca	0.04	94	0.04	0.01	0.1	0.03	0.1	0.02
Zn	0.04	94	0.03	0.002	0.2	0.01	0.1	0.04
Cr	0.01	94	0.01	0	0.03	0.01	0.01	0.01
Ni	0.01	94	0.005	0	0.02	0.003	0.01	0.003
Al	0.03	94	0.02	0	0.2	0.01	0.04	0.02
NH ₄ ⁺	0.4	94	0.3	0.01	1.2	0.2	0.6	0.3
NO ₃ ⁻	0.8	94	0.7	0.02	2.3	0.5	1.0	0.4
SO ₄ ²⁻	1.3	94	1.1	0.4	2.7	0.9	1.6	0.5
EC	6.6	94	5.1	1.1	27.3	3.1	8.7	5.1
BC	7.0	94	5.2	0.8	22.7	3.2	9.8	5.0
OC _{mass}	7.0	94	5.4	2.0	22.9	3.7	9.1	4.3
PM _{2.5}	27.7	94	20.9	2.2	96.3	11.9	37.5	21.0

OC_{mass} = estimated organic carbon mass

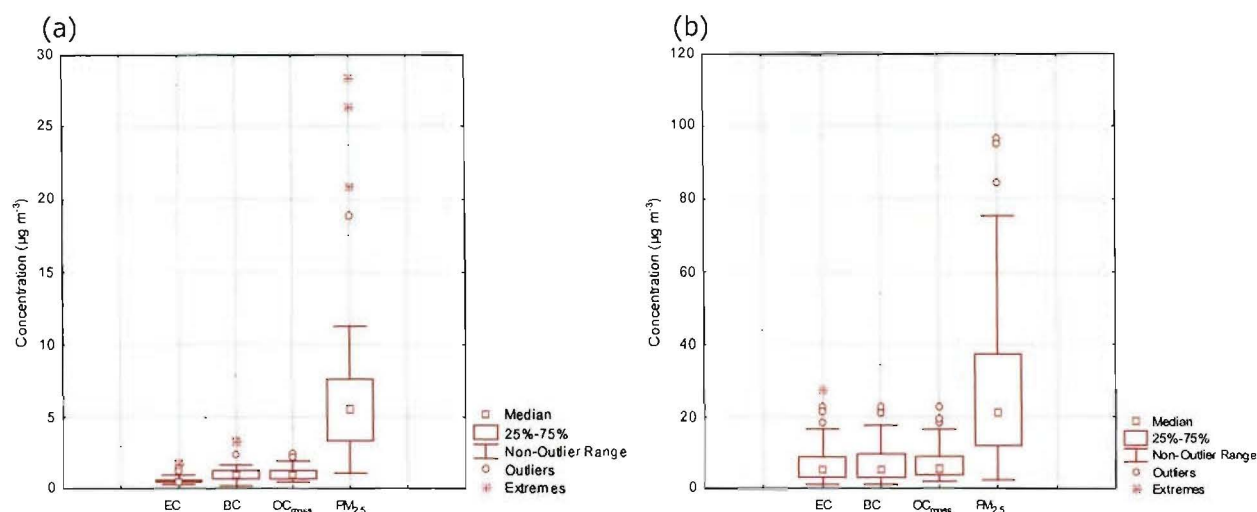


Figure 7.1 Distribution of 24-hour average $PM_{2.5}$ and major chemical constituents in (a) summer and (b) winter, Christchurch, 2001/2002.

OC, EC (and BC) were the main chemical constituents of $PM_{2.5}$, with substantially lower concentrations evident in summer. BC was more widely distributed than EC and OC_{mass} in summer, while in winter, EC concentrations were greater than OC_{mass} and BC. The distributions of the remaining elemental and ion species are presented in Figure 7.2a and b. The most abundant species present in summer, other than the carbon compounds, were sulphate followed by sodium, chlorine, sulphur, nitrate and ammonium. These species, together with potassium, were also prominent in the winter months.

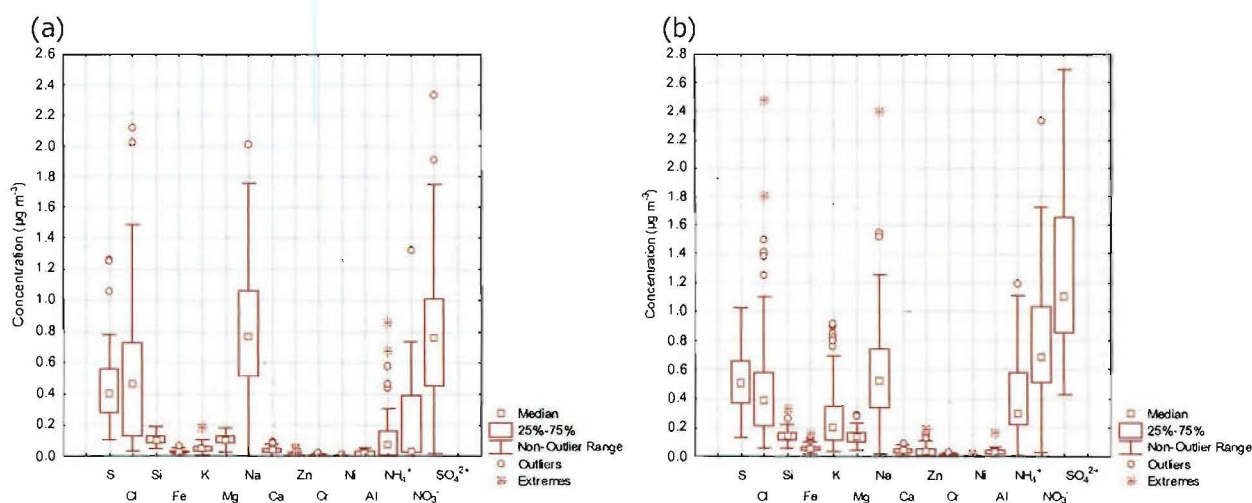


Figure 7.2 Distribution of key chemical constituents of 24-hour average $PM_{2.5}$ in (a) summer and (b) winter, Christchurch, 2001/2002.

7.2 Fine particle concentrations

Figure 7.3 presents PM_{2.5} concentrations measured from November 2001 to March 2002, and May to August 2002 (samples were not collected for the period from 21 December 2001 to 15 January 2002). Fine particles in Christchurch were seasonally distributed, with higher concentrations evident during the wintertime.

During summer, higher concentrations occurred towards the cooler end of the season (March). The summertime maximum concentration of 28.3 $\mu\text{g m}^{-3}$ was measured late summer, on 28 March 2002. The median was 5.5 $\mu\text{g m}^{-3}$ with 75% of data below 7.6 $\mu\text{g m}^{-3}$. The PM_{2.5} concentrations observed in summer were relatively low compared with those indicated in studies overseas. For example, Brook and Dann (1999) reported summer medians across Canada in the range of 5 to 16 $\mu\text{g m}^{-3}$, and Chow *et al.* (1994) observed maxima between 36.4 and 63.7 $\mu\text{g m}^{-3}$ in California.

Fine particle concentrations were elevated during the winter months. The maximum concentration measured was 96.3 $\mu\text{g m}^{-3}$, which occurred on 22 May 2002. The median concentration was 20.9 $\mu\text{g m}^{-3}$ with 75% of data below 37.5 $\mu\text{g m}^{-3}$. Peaks were most evident from May to early June, with lower concentrations observed from mid-July. The pattern reflects meteorological conditions during the 2002 winter, when the coolest weather occurred during May and June, with milder, cloudier weather in July and August.

Studies including Cohen (1999), Brook *et al.* (1997), Chan *et al.* (1997), Chow *et al.* (1993), and Castanho and Artaxo (2001) also observed seasonal patterns in PM_{2.5} concentrations. Chow *et al.* (1993) found that PM_{2.5} concentrations more than doubled in late autumn and winter at most sites in the San Joaquin Valley. Maximum values in the range of 64 to 164 $\mu\text{g m}^{-3}$ and arithmetic averages of 19 to 36 $\mu\text{g m}^{-3}$ were measured during that study. Higher PM_{2.5}/PM₁₀ ratios during the winter months were also reported, suggesting an increase in the contributions of combustion sources at that time of year (Brook *et al.*, 1997; Chow *et al.*, 1993; Chow *et al.*, 1994).

The PM_{2.5} concentrations measured in Christchurch were evaluated against the recommended monitoring value proposed by New Zealand's MfE (25 $\mu\text{g m}^{-3}$, 24-hour average). Although PM_{2.5} guidelines are normally attained in summer, there were two exceedences of the MfE monitoring value in 2002. Both exceedences occurred in March and it is likely that outdoor burning activities, common at that time of the year, were responsible for the high concentrations. During the winter, the MfE monitoring value was exceeded on 42 of the 94 wintertime sampling days (45%). The number of exceedences recorded would have been greater if sampling had been conducted every day (rather than 5 to 6 days per week), and if the 11 high pollution days eliminated from the analysis due to filter blockages had been included. Whilst the magnitude and number of exceedences is of concern, the extended period of time when people are exposed to these concentrations is also significant.

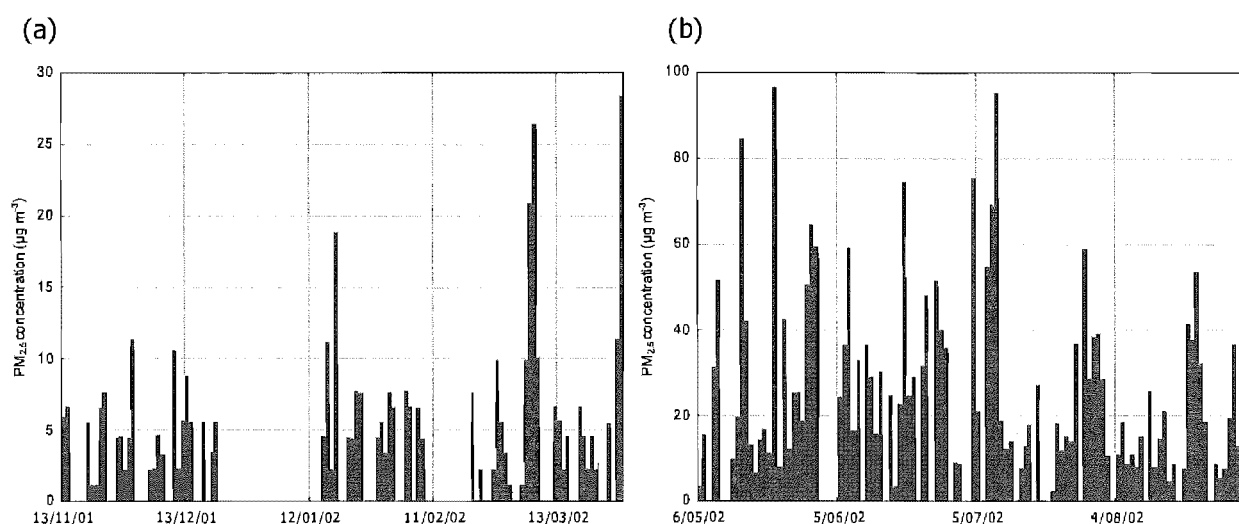


Figure 7.3 24-hour average PM_{2.5} concentrations in (a) summer and (b) winter, Christchurch, 2001/2002. NB: Difference in the Y-axis scales.

7.3 Elemental/black carbon and organic carbon mass

Figure 7.4 to Figure 7.6 present carbon concentrations from November 2001 to March 2002, and May to August 2002. These include OC_{mass}, BC and EC. The patterns of concentrations were similar to PM_{2.5} with peak measurements occurring in the winter. Carbon concentrations were generally below 3.5 µg m⁻³ in the summer, but up to 28 µg m⁻³ in the winter. Seasonal patterns in OC and EC concentrations have also been observed elsewhere (Tropp *et al.*, 2002; Castanho and Artaxo, 2001; Chow *et al.*, 1994; Lee and Kang, 2001; Sun *et al.*, 2004; Ward *et al.*, 2004). Castanho and Artaxo (2001), for example, reported summertime averages of 4.1 µg m⁻³ for EC and 5.3 µg m⁻³ for OC, and wintertime averages of 7.6 µg m⁻³ for EC and 15.8 µg m⁻³ for OC, in Sao Paulo, Brazil.

In the summer, the maximum OC_{mass} concentration of 2.4 µg m⁻³ occurred on 28 November 2001. The median OC_{mass} concentration was 0.9 µg m⁻³, with 75% of data below 1.2 µg m⁻³. The maximum EC concentration of 1.7 µg m⁻³ occurred on 8 March 2002. The median EC concentration was 0.5 µg m⁻³ with 75% of data below 0.6 µg m⁻³. The maximum OC_{mass} and EC concentrations were lower than those reported for California, where maximum summertime OC concentrations were in the range of 5.3 to 11 µg m⁻³, and EC from 1.9 to 5.4 µg m⁻³ (Chow *et al.*, 1994). The BC maximum of 3.4 µg m⁻³ occurred on 18 March 2002. This was greater than maximum OC_{mass}, contrary to that demonstrated elsewhere, where higher concentrations of OC than EC (or BC) are generally reported (e.g. Ito *et al.*, 2004; Chow *et al.*, 1993). The median BC concentration was 0.9 µg m⁻³ with 75% of data below 1.3 µg m⁻³.

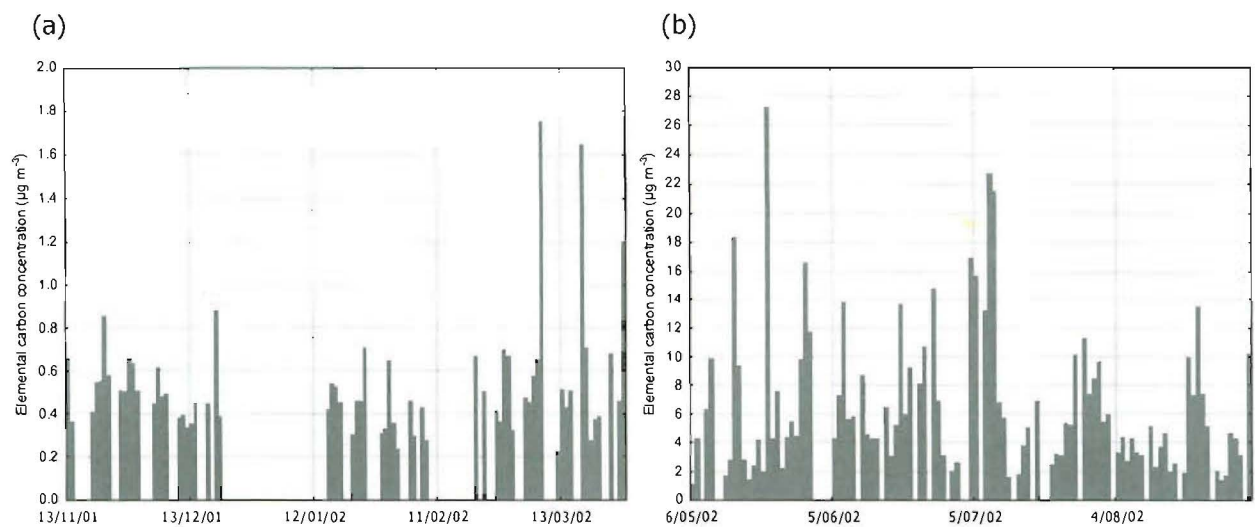


Figure 7.4 24-hour average EC concentrations in (a) summer and (b) winter, Christchurch, 2001/2002. NB: Differences in the Y-axis scales.

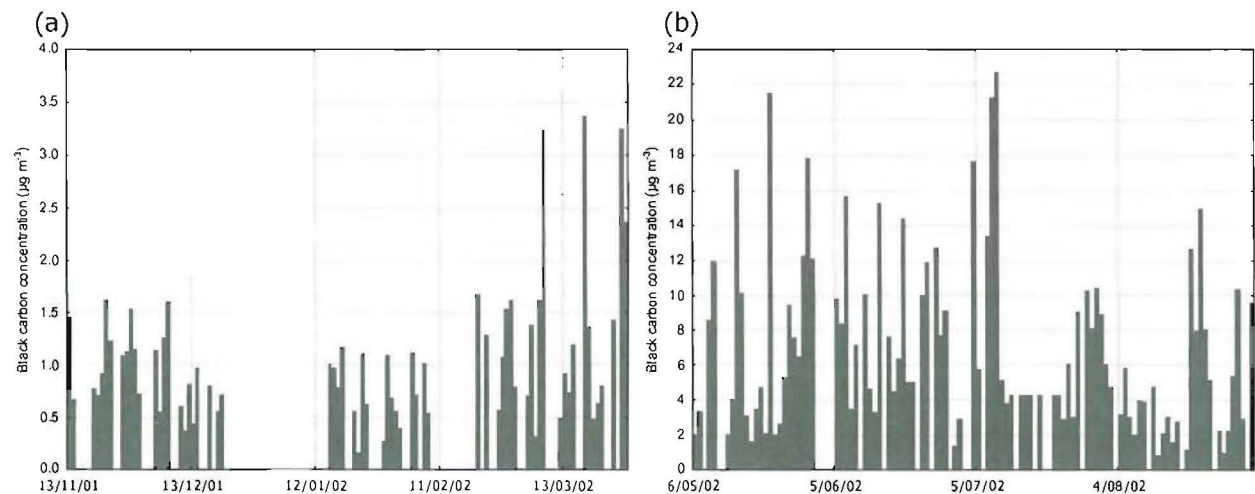


Figure 7.5 24-hour average BC concentrations in (a) summer and (b) winter, Christchurch, 2001/2002. NB: Differences in the Y-axis scales.

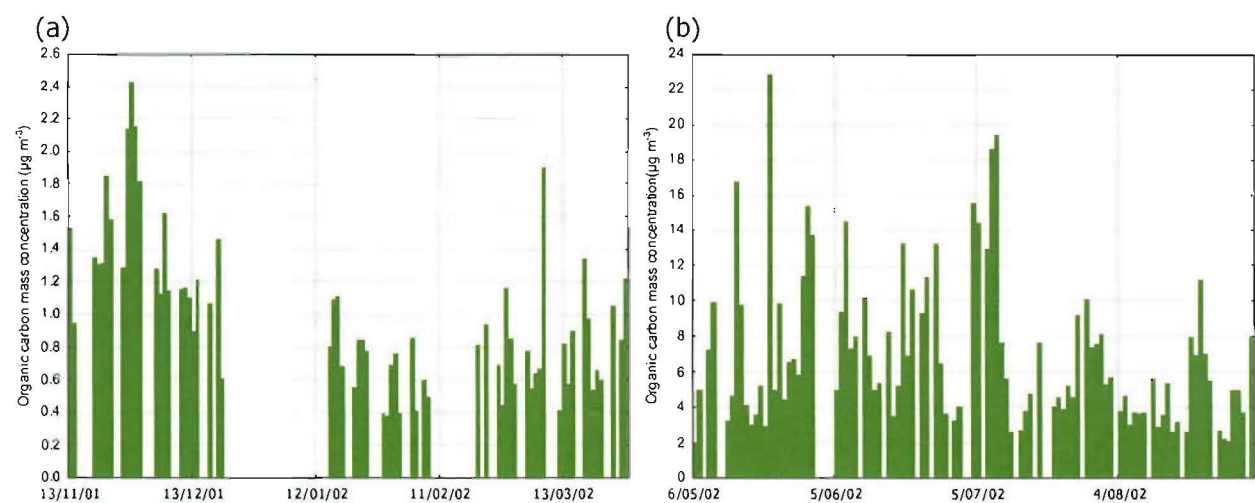


Figure 7.6 24-hour average OC_{mass} concentrations in (a) summer and (b) winter, Christchurch, 2001/2002. NB: Differences in the Y-axis scales.

In winter, the maximum OC_{mass} concentration of $22.9 \mu g m^{-3}$ occurred on 22 May 2002, coinciding with the peak $PM_{2.5}$ value. The median OC_{mass} concentration was $5.4 \mu g m^{-3}$ with 75% of data below $9.1 \mu g m^{-3}$. The maximum EC concentration of $27.3 \mu g m^{-3}$ also occurred on 22 May 2002. The median EC concentration was $5.1 \mu g m^{-3}$ with 75% of data below $8.7 \mu g m^{-3}$. While maximum OC_{mass} was of a similar magnitude to those detected during the autumn months in California (21 to $33 \mu g m^{-3}$), the maximum EC concentration was significantly higher (e.g. a maximum concentration of $12.1 \mu g m^{-3}$ was measured in Los Angeles; Chow *et al.*, 1994). BC had a maximum concentration of $22.7 \mu g m^{-3}$ (lower than maximum EC), and occurred on a different day to the OC and EC maxima (9 July 2002). The median BC concentration was $5.2 \mu g m^{-3}$ with 75% of data below $9.8 \mu g m^{-3}$. Again, it is important to note that the EC and BC maxima were greater than that observed for OC, when OC_{mass} is converted back to OC. These measurements suggest that either sources in Christchurch discharge different quantities of OC to EC than elsewhere, or, and more likely, that there is an issue associated with the OC and EC measurements.

OC and EC were measured continuously using an R&P Series 5400 ambient carbon particulate monitor, and BC by light reflection/transmission. An investigation of the monitoring records revealed that the temperature setting used by the Series 5400 to differentiate between OC and EC ($230^{\circ}C$) during the study was different to that recommended by the instrument manufacturer ($340^{\circ}C$). Assuming that the Series 5400 at $340^{\circ}C$ produces equivalent results to other methods reported in the literature,³⁹ it is likely that the lower differentiation temperature ($230^{\circ}C$) would underestimate OC and overestimate EC, relative to other measurements. Concerns regarding these measurements led to an additional investigation of OC and EC in Christchurch (winter 2004). This is addressed in detail in Chapter 8. In the interim, as a consequence of the uncertainties associated with the Series 5400 data, BC was selected as the primary carbon species for the receptor modelling. As it was important to account for as much $PM_{2.5}$ mass as possible, the Series 5400 OC_{mass} measurements were also included as a separate species in the modelling. It was understood that the underestimated OC_{mass} concentrations could potentially lead to an underestimate of the source contributions.

7.4 Inorganic ions

Figure 7.7 to Figure 7.9 present inorganic ion concentrations from November 2001 to March 2002, and May to August 2002.⁴⁰ Seasonal trends are apparent with greater concentrations in the winter months. However, several sulphate events also occurred in the summer.

³⁹ The most common partitioning temperature used to distinguish between OC and EC in the literature is $550^{\circ}C$, although this is for a filter-based analytical technique (Park *et al.*, 2001; Pryor *et al.*, 1997; Eldred *et al.*, 1997; Lee and Kang, 2001).

⁴⁰ For receptor modelling purposes, substituted values were used for missing data (see Chapter 6 and Appendix 2). These are particularly evident in the wintertime ion concentrations. Five-day sampling was conducted in winter for these species while the other elements (i.e. measured by PIXE) were sampled six days per week. Therefore, it was necessary for data to be substituted into the dataset every sixth day. This explains the repeating values evident throughout the dataset.

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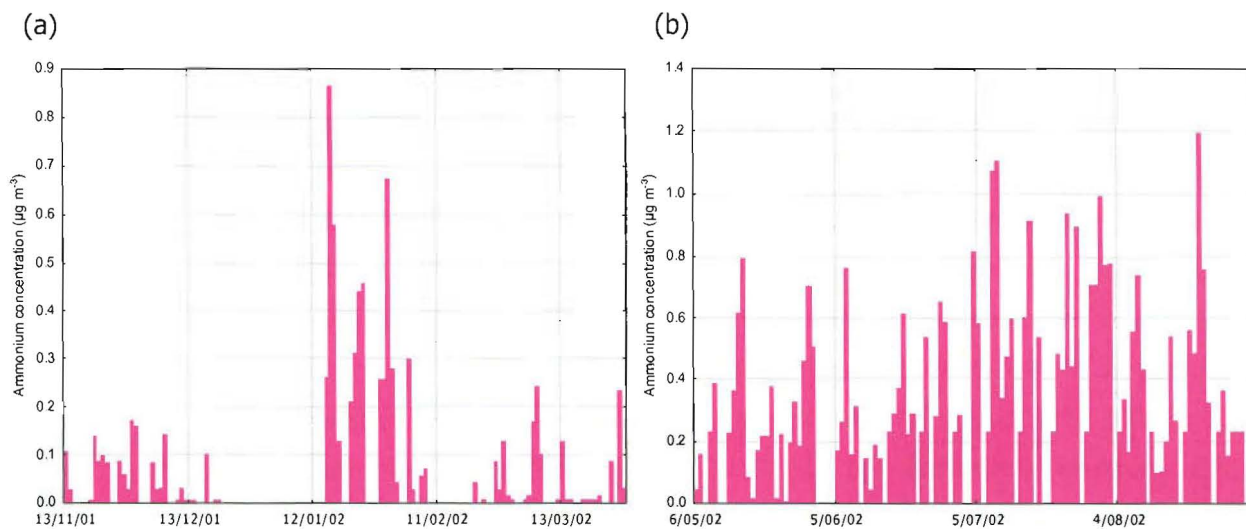


Figure 7.7 24-hour average ammonium concentrations in (a) summer and (b) winter, Christchurch, 2001/2002. Note: Difference in Y-axis scale.

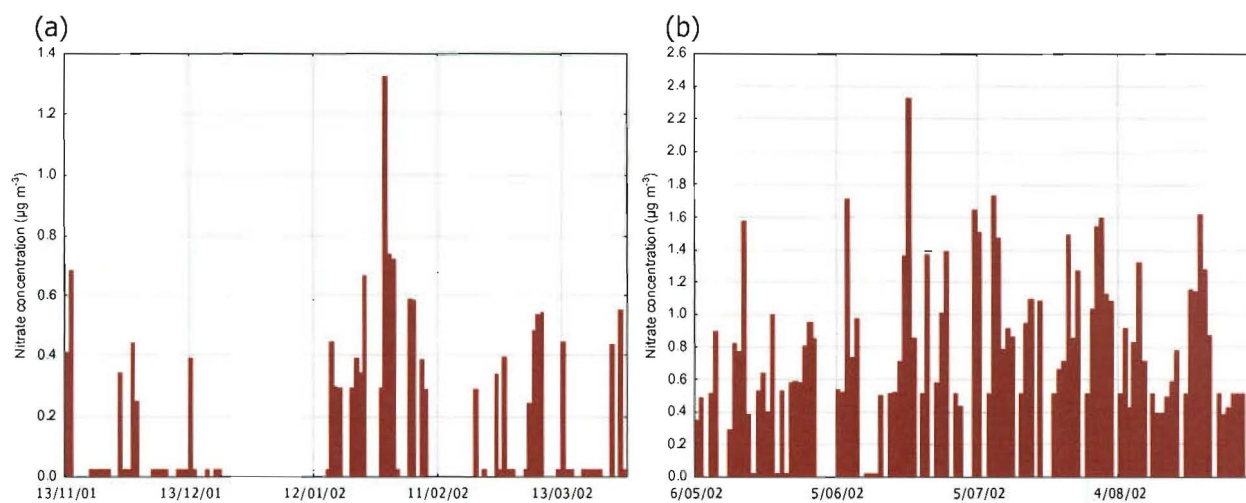


Figure 7.8 24-hour average nitrate concentrations in (a) summer and (b) winter, Christchurch, 2001/2002. Note: Difference in Y-axis scale.

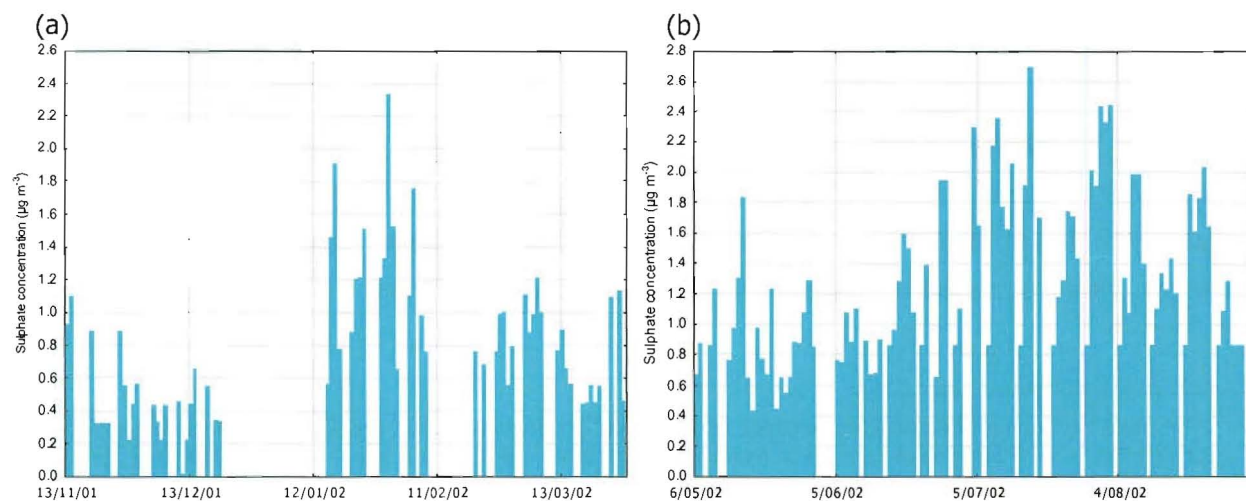


Figure 7.9 24-hour average sulphate concentrations in (a) summer and (b) winter, Christchurch, 2001/2002.

During summer, sulphate was consistently more abundant than nitrate, and nitrate greater than ammonium. The exception was an ammonium peak, which occurred on 16 January 2001. The maximum sulphate concentration of $2.3 \mu\text{g m}^{-3}$ occurred on 30 January 2002, which coincided with the peak sulphur concentration and the chlorine minimum. Photochemical processes at the coast may have led to the formation of Na_2SO_4 on that day, as H_2SO_4 neutralised by NaCl can deplete chlorine concentrations (Polissar *et al.*, 2001; Chow and Watson, 1998). The median sulphate concentration was $0.8 \mu\text{g m}^{-3}$ with 75% of data below $1 \mu\text{g m}^{-3}$. The maximum nitrate concentration of $1.3 \mu\text{g m}^{-3}$ occurred on 29 January 2002. The median nitrate concentration was $0.02 \mu\text{g m}^{-3}$ with 75% of data below $0.4 \mu\text{g m}^{-3}$. The maximum ammonium concentration of $0.9 \mu\text{g m}^{-3}$ occurred on 16 January 2002 and coincided with a sulphur peak. It is likely that significant quantities of SO_2 were available on that day to react with NH_3 , in the presence of water and an oxidant, to form $(\text{NH}_4)_2\text{SO}_4$. The median ammonium concentration was $0.1 \mu\text{g m}^{-3}$ with 75% of data below $0.2 \mu\text{g m}^{-3}$.

The summertime ion concentrations in Christchurch were low relative to those observed in California and Chongju, Korea. Chow *et al.* (1994) reported summer sulphate maxima in the range of 10 to $19 \mu\text{g m}^{-3}$, and nitrate maxima between 2.3 and $10 \mu\text{g m}^{-3}$ in California, while Lee and Kang (2001) detected sulphate and ammonium means of $9.8 \mu\text{g m}^{-3}$ and $3.1 \mu\text{g m}^{-3}$ in Chongju, South Korea.

The relative concentrations of the inorganic ion species were more variable in winter. Although sulphate concentrations were normally greater than nitrate and ammonium, nitrate concentrations occasionally exceeded sulphate. The maximum sulphate concentration of $2.7 \mu\text{g m}^{-3}$ occurred on 16 July 2002. The median sulphate concentration was $1.1 \mu\text{g m}^{-3}$ with 75% of data below $1.6 \mu\text{g m}^{-3}$. Sulphate concentrations were lower in early winter and increased steadily from late June. This suggested that milder weather evident in July and August may have been more conducive to photochemical activity. The maximum nitrate concentration of $2.3 \mu\text{g m}^{-3}$ occurred on 20 June 2002. The median nitrate concentration was $0.7 \mu\text{g m}^{-3}$ with 75% of data below $1 \mu\text{g m}^{-3}$. The maximum ammonium concentration of $1.2 \mu\text{g m}^{-3}$ occurred on 21 August 2002, while the median ammonium concentration was $0.3 \mu\text{g m}^{-3}$ with 75% of data below $0.6 \mu\text{g m}^{-3}$.

Seasonal patterns in sulphate concentrations are commonly reported in the literature, although concentrations are usually higher during the warmer months of the year (Tropp *et al.*, 2002; Chan *et al.*, 1997; Chow *et al.*, 1994). However, Park *et al.* (2001) observed higher sulphate concentrations in the winter, with an average of $5.3 \mu\text{g m}^{-3}$. The concentrations measured in Christchurch, when evaluated against those reported elsewhere, were relatively low. Lee and Kang (2001) detected mean wintertime concentrations of $5.8 \mu\text{g m}^{-3}$ in Chongju, South Korea, and Chow *et al.* (1994) recorded autumn maxima of 8.2 to $9.8 \mu\text{g m}^{-3}$ in California. In Christchurch, sulphate concentrations are higher in winter, as the concentration of precursors available for reaction is greatest under temperature inversion conditions.

Wintertime peaks in nitrate concentrations are widely reported (Brook and Dann, 1999; Lee and Kang, 2001; Tropp *et al.*, 2002; Brook *et al.*, 1997; Park *et al.*, 2001 and Chow *et al.*, 1994). Nitrate production is directly related to temperature as this determines whether nitrate will be present in a gaseous or particulate form. At temperatures greater than 15 to 20°C most nitrate is present as a gas, and below this range, nitrate is predominantly available as fine particles (Seidl *et al.*, 1996 as cited in Meszaros, 1999). Brook and Dann (1999), for example, found approximately 10 to 25% more nitrate present in the particle phase during Canada's cold season than in the warmer months of the year. Although nitrate concentrations in Christchurch were highest in the winter, the measurements were still low relative to other studies. Chow *et al.* (1994) observed substantially higher nitrate concentrations in California, with maxima between 30.6 and 74 $\mu\text{g m}^{-3}$ measured during the autumn months.

Seasonal trends in ammonium concentrations have also been reported internationally (Chow *et al.*, 1994; Park *et al.*, 2001). Chow *et al.* (1994) measured maximum ammonium concentrations of 3.5 to 7.9 $\mu\text{g m}^{-3}$ in California in the summer and 11.5 to 23.5 $\mu\text{g m}^{-3}$ in autumn. The concentrations measured in Christchurch were substantially lower than these Californian measurements.

7.5 Major elements

Figure 7.10 to Figure 7.13 present concentrations of major elemental species from November 2001 to March 2002, and May to August 2002. Of these chemical species, potassium is the only element that exhibits a strong seasonal trend, with substantially higher concentrations in the winter months. Sulphur concentrations, while also higher in winter, peaked occasionally during summer. These peaks coincided with sulphate concentrations suggesting that photochemical processes were active at that time. Concentrations of sodium and chlorine, on the other hand, were slightly lower during the winter. Seasonal patterns in sulphur and potassium concentrations have also been observed elsewhere. Chow *et al.* (1994) found slightly higher sulphur maximum concentrations in the summer (3 to 5 $\mu\text{g m}^{-3}$) than in autumn (3 to 4 $\mu\text{g m}^{-3}$), and Castanho and Artaxo (2001) observed higher potassium concentrations during the winter, reporting an average of 0.1 $\mu\text{g m}^{-3}$ in summer and 0.4 $\mu\text{g m}^{-3}$ in winter.

In Christchurch, higher summertime concentrations were usually associated with marine aerosol or photochemical events. The maximum sulphur concentration of 1.3 $\mu\text{g m}^{-3}$ occurred on 16 January 2002. The median sulphur concentration was 0.4 $\mu\text{g m}^{-3}$ with 75% of data below 0.6 $\mu\text{g m}^{-3}$. Sulphur peaks, such as those occurring on 16 and 30 January 2002, often coincided with low chlorine and sodium concentrations. The minimum chlorine value (0.03 $\mu\text{g m}^{-3}$), which occurred on 30 January 2002, corresponded with the second sulphur peak. Atmospheric chemistry was clearly important on these days (Section 2.2.2). The maximum chlorine concentration of 2.1 $\mu\text{g m}^{-3}$ occurred on 5 March 2002. The median chlorine concentration was 0.5 $\mu\text{g m}^{-3}$ with 75% of data below 0.7 $\mu\text{g m}^{-3}$. The maximum sodium concentration of 2.0 $\mu\text{g m}^{-3}$ occurred on 5 March 2003. This corresponded with the

highest chlorine value, highlighting a potential link between emissions of these substances. The median sodium concentration was $0.8 \mu\text{g m}^{-3}$ with 75% of data below $1.1 \mu\text{g m}^{-3}$.

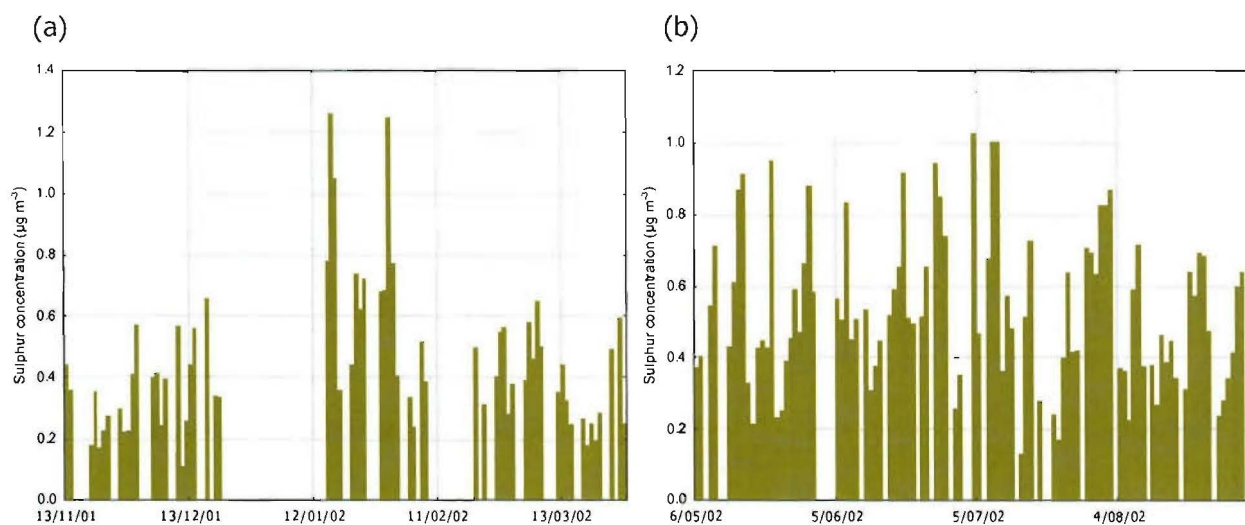


Figure 7.10 24-hour average sulphur concentrations in (a) summer and (b) winter, Christchurch, 2001/2002.

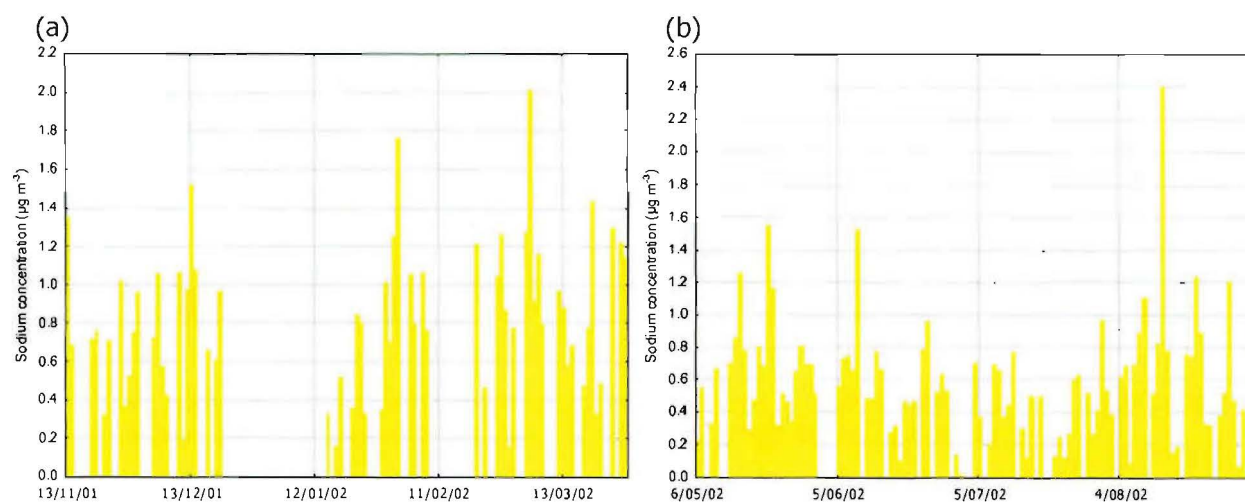


Figure 7.11 24-hour average sodium concentrations in (a) summer and (b) winter, Christchurch, 2001/2002.

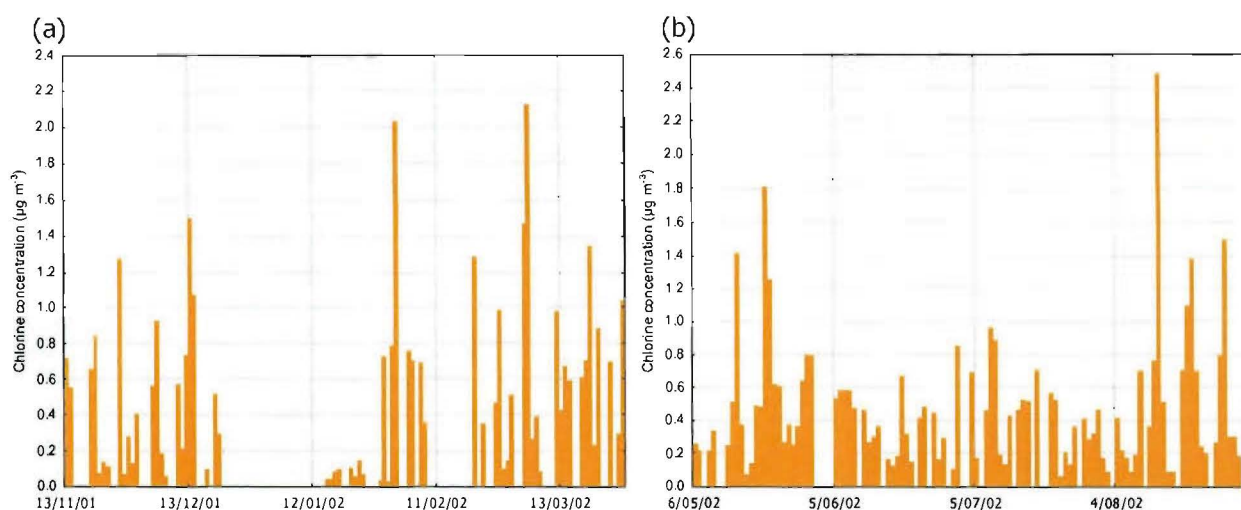


Figure 7.12 24-hour average chlorine concentrations in (a) summer and (b) winter, Christchurch, 2001/2002.

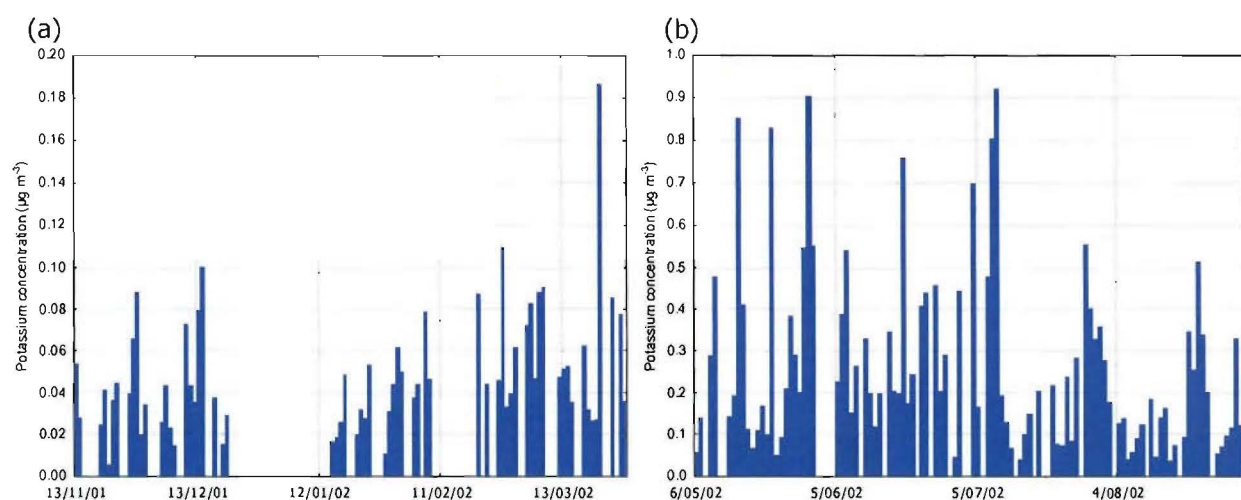


Figure 7.13 24-hour average potassium concentrations in (a) summer and (b) winter, Christchurch, 2001/2002. NB: Difference in Y-axis scales.

A comparison of the summertime measurements with those reported in California, indicate lower sulphur, and higher sodium and chlorine concentrations in Christchurch. Chow *et al.* (1994) measured maximum sulphur concentrations in the range of 3 to 5 $\mu\text{g m}^{-3}$ (various sites), and sodium and chlorine concentrations of 0.5 $\mu\text{g m}^{-3}$ and 0.2 $\mu\text{g m}^{-3}$ at Long Beach, California.

The wintertime measurements in Christchurch were characterised by a greater abundance of potassium and isolated sodium and chlorine events. Potassium concentrations were substantially higher in the winter and were greatest in May and June. Peaks were not as frequent during the months of July and August, as was the case for OC_{mass} and EC. The maximum potassium concentration of 0.9 $\mu\text{g m}^{-3}$ occurred on 9 July 2002, coinciding with the BC peak. This suggests that potassium and BC may be linked. However, potassium is an indicator of wood smoke and while a

relationship with carbon is expected, stronger associations should occur with OC_{mass} rather than BC. Again, this supports the view that there is considerable uncertainty associated with the OC_{mass} measurements, or alternatively, that combustion sources in New Zealand discharge higher quantities of EC relative to OC_{mass} . The median potassium concentration was $0.2 \mu\text{g m}^{-3}$ with 75% of data below $0.3 \mu\text{g m}^{-3}$. The maximum sulphur concentration of $1 \mu\text{g m}^{-3}$ occurred on 4 July 2002. The median sulphur concentration was $0.5 \mu\text{g m}^{-3}$ with 75% of data below $0.7 \mu\text{g m}^{-3}$. Sulphur concentrations throughout the winter period were relatively consistent, ranging from 0.1 to $1 \mu\text{g m}^{-3}$. Chlorine and sodium concentrations were relatively low in the winter, although several significant events were evident. The maximum chlorine concentration of $2.5 \mu\text{g m}^{-3}$, measured on 13 August 2002, was higher than the summertime maximum. The median chlorine concentration was $0.4 \mu\text{g m}^{-3}$ with 75% of data below $0.6 \mu\text{g m}^{-3}$. The maximum sodium concentration of $2.4 \mu\text{g m}^{-3}$ also occurred on 13 August 2002, suggesting that marine aerosol was present on that day. The median sodium concentration was $0.5 \mu\text{g m}^{-3}$ with 75% of data under $0.7 \mu\text{g m}^{-3}$.

Maximum wintertime concentrations of sodium, chlorine and potassium in Christchurch were greater than autumn measurements observed in California. Chow *et al.* (1994) reported maximum concentrations of $1.7 \mu\text{g m}^{-3}$ and $0.3 \mu\text{g m}^{-3}$ at Long Beach for chlorine and sodium, and 0.3 to $0.4 \mu\text{g m}^{-3}$ for potassium. Conversely, the sulphate measurements in Christchurch were lower than those found in California, where autumn maxima in the range of 3.4 to $4.2 \mu\text{g m}^{-3}$ were detected (Chow *et al.*, 1994).

7.6 Relationships between chemical species

Relationships between the individual species were determined by conducting a Spearman R correlation analysis. This provided an initial overview of potential elemental groupings and sources. The primary focus was on the entire dataset, as a maximum number of samples is required for receptor modelling to be successful. Nevertheless, some discussion of differences in species relationships on a seasonal basis is included. The results of the analysis of the total dataset are presented in Table 7.2.

The coefficients in Table 7.2 demonstrate the significance of combustion related species in Christchurch and their inter-relationships. Strong correlations were evident between the carbon compounds, iron, potassium and zinc. Relationships between secondary particulate species were also strong, with coefficients of 0.85 for ammonium and nitrate, 0.79 for ammonium and sulphate and 0.8 for sulphate and nitrate. Associations between non-combustion related chemical species such as those found in marine aerosol and soil, were not as distinctive. However, the marine aerosol constituents were negatively correlated with many species including OC_{mass} , EC/BC, silicon, chromium, nickel, aluminium, ammonium, nitrate and sulphate. This was related to differences in the meteorological conditions under which wintertime combustion and summertime marine aerosol occur. In winter, conditions are stable and emissions accumulate, and the winds are generally light and offshore. Conversely, in summer wind speeds are elevated, wind direction is more frequently onshore

Table 7.2 Relationship between chemical species, Spearman R correlation coefficients, Christchurch, 2001/2002.

Species	S	Cl	Si	Fe	K	Mg	Na	Ca	Zn	Cr	Ni	Al	NH ₄ ⁺	NO ₃ ⁻	SO ₄ ²⁻	EC	BC	OC _{mass}	PM _{2.5}
S	1																		
Cl	-0.07	1																	
Si	0.40	-0.05	1																
Fe	0.44	0.08	0.69	1															
K	0.49	0.22	0.50	0.75	1														
Mg	0.22	0.37	0.20	0.33	0.32	1													
Na	0.12	0.60	-0.19	-0.12	-0.04	0.25	1												
Ca	0.36	0.53	0.19	0.28	0.36	0.40	0.45	1											
Zn	0.51	0.06	0.52	0.71	0.75	0.18	-0.13	0.28	1										
Cr	0.04	-0.14	0.25	0.42	0.32	0.21	-0.29	-0.09	0.21	1									
Ni	0.09	-0.01	0.23	0.32	0.30	0.26	-0.20	0.08	0.25	0.28	1								
Al	0.18	-0.02	0.46	0.39	0.22	0.23	-0.09	0.16	0.25	0.17	0.09	1							
NH ₄ ⁺	0.66	-0.19	0.51	0.59	0.53	0.28	-0.21	0.09	0.58	0.32	0.26	0.19	1						
NO ₃ ⁻	0.57	-0.03	0.48	0.63	0.62	0.32	-0.07	0.17	0.60	0.31	0.22	0.26	0.85	1					
SO ₄ ²⁻	0.59	-0.04	0.39	0.46	0.41	0.37	0.00	0.20	0.41	0.32	0.19	0.21	0.79	0.80	1				
EC	0.42	0.01	0.51	0.77	0.84	0.32	-0.22	0.22	0.76	0.41	0.34	0.26	0.67	0.70	0.46	1			
BC	0.44	0.04	0.50	0.81	0.87	0.22	-0.19	0.26	0.79	0.37	0.32	0.24	0.61	0.67	0.41	0.92	1		
OC _{mass}	0.36	0.02	0.50	0.76	0.83	0.26	-0.24	0.20	0.72	0.40	0.30	0.27	0.60	0.64	0.36	0.97	0.91	1	
PM _{2.5}	0.51	0.12	0.47	0.72	0.82	0.28	0.01	0.31	0.69	0.28	0.24	0.22	0.59	0.68	0.45	0.84	0.84	0.82	1

NB: Coefficients greater than 0.7 and significant at p<0.05 are highlighted

and emissions are dispersed. Contaminants are not as concentrated under summertime conditions and are more difficult to detect. Subsequently, relationships between species may be less distinct than those evident during the winter. Examination of the summer and wintertime relationships demonstrates that this may have been the case.

When the summer and winter datasets were analysed separately, it was found that the greatest summertime associations were between the constituents of marine aerosol. That is, sodium, chlorine, calcium and magnesium. Sodium and chlorine had the strongest relationship with a coefficient of 0.73, followed by sodium and magnesium (0.68), nitrate and sulphate (0.68), sodium and calcium (0.65), and sulphur and sulphate (0.63). Combustion species were poorly correlated and appeared to be unrelated in the summer dataset. This lack of correlation was not unexpected as easterly winds from the coast, predominant at that time of the year, substantially dilute contaminant concentrations.

Associations between soil-related species such as silicon, iron, aluminium and ammonium were absent from the summer dataset. Northwesterly winds, also relatively frequent during the summer, are expected to transport soil particles from surrounding farmland to Christchurch. While most soil-related particles are larger than $PM_{2.5}$, soil sources are readily resolved in similar studies of $PM_{2.5}$ conducted overseas (e.g. Ramadan *et al.*, 2000; Polissar *et al.*, 1998; Maykut *et al.*, 2003; Polissar *et al.*, 2001; Song *et al.*, 2001; Poirot *et al.*, 2001). Potential reasons for the lack of association between soil-related species may be that winds during the two study periods were not of adequate strength or duration to transport soil particles to the receptor site, or alternatively, that concentrations of the soil-related compounds were insufficient to allow relationships to be established.

During the winter months, combustion related species and secondary particulate compounds had the greatest associations. The carbon compounds were most strongly associated with $PM_{2.5}$ (0.88 to 0.90), followed by potassium (0.85). Again, there was a more notable link between potassium and BC (0.9) than with OC_{mass} (0.84). This is a reflection of the measurement issues associated with the carbon data, as discussed later in Chapter 8. Strong correlations were also evident between secondary particulate species, with a coefficient of 0.86 derived for ammonium and nitrate, 0.8 for ammonium and sulphate, and 0.78 for nitrate and sulphate. This suggests that compounds such as NH_4NO_3 and $(NH_4)_2SO_4$ were important $PM_{2.5}$ constituents during the winter months.

Analysis of the separate datasets also revealed that elements such as sulphur may be associated with different sources at certain times of the year. In summer, sulphur was associated with sulphate (0.63), and in winter was linked to potassium (0.73), BC (0.73), zinc (0.75) and, to a lesser extent OC_{mass} (0.61) and $PM_{2.5}$ (0.68). This suggested that during the warmer months of the year sulphur was predominantly present in the secondary sulphate form, but in winter as primary sulphur discharged from combustion. Relationships with sulphur were substantially weaker when the entire

dataset was analysed. Therefore, receptor modelling on a seasonal basis may be more appropriate for the accurate determination of sulphur sources.

A series of scatter plots (and histograms) have been compiled to visually represent the inter-relationships of highly correlated species for the combined dataset. These are presented in Figure 7.14. The corresponding r^2 and r values, all significant at $p < 0.05$, are outlined in Table 7.3. These are ranked in order of strength and confirm that the strongest relationships exist between the carbon species, potassium and iron.

Table 7.3 Key elemental relationships (see also Figure 7.14), Christchurch, 2001/2002.

Relationships between species	r^2	r	Relationships between species	r^2	r
EC/OC _{mass}	0.96	0.98	NH ₄ ⁺ /SO ₄ ²⁻	0.70	0.83
K/BC	0.88	0.94	NH ₄ ⁺ /NO ₃ ⁻	0.67	0.82
BC/PM _{2.5}	0.87	0.93	Fe/OC _{mass}	0.66	0.81
K/PM _{2.5}	0.86	0.93	Zn/BC	0.62	0.79
EC/PM _{2.5}	0.86	0.93	Fe/PM _{2.5}	0.62	0.79
EC/BC	0.85	0.92	NO ₃ ⁻ /SO ₄ ²⁻	0.62	0.79
OC _{mass} /PM _{2.5}	0.85	0.92	Fe/K	0.61	0.78
BC/OC _{mass}	0.84	0.92	K/Zn	0.60	0.78
K/OC _{mass}	0.83	0.91	Fe/Zn	0.56	0.75
K/EC	0.83	0.91	Zn/EC	0.56	0.75
Fe/EC	0.71	0.84	Zn/OC _{mass}	0.53	0.73
Fe/BC	0.71	0.84	NO ₃ ⁻ /EC	0.42	0.65

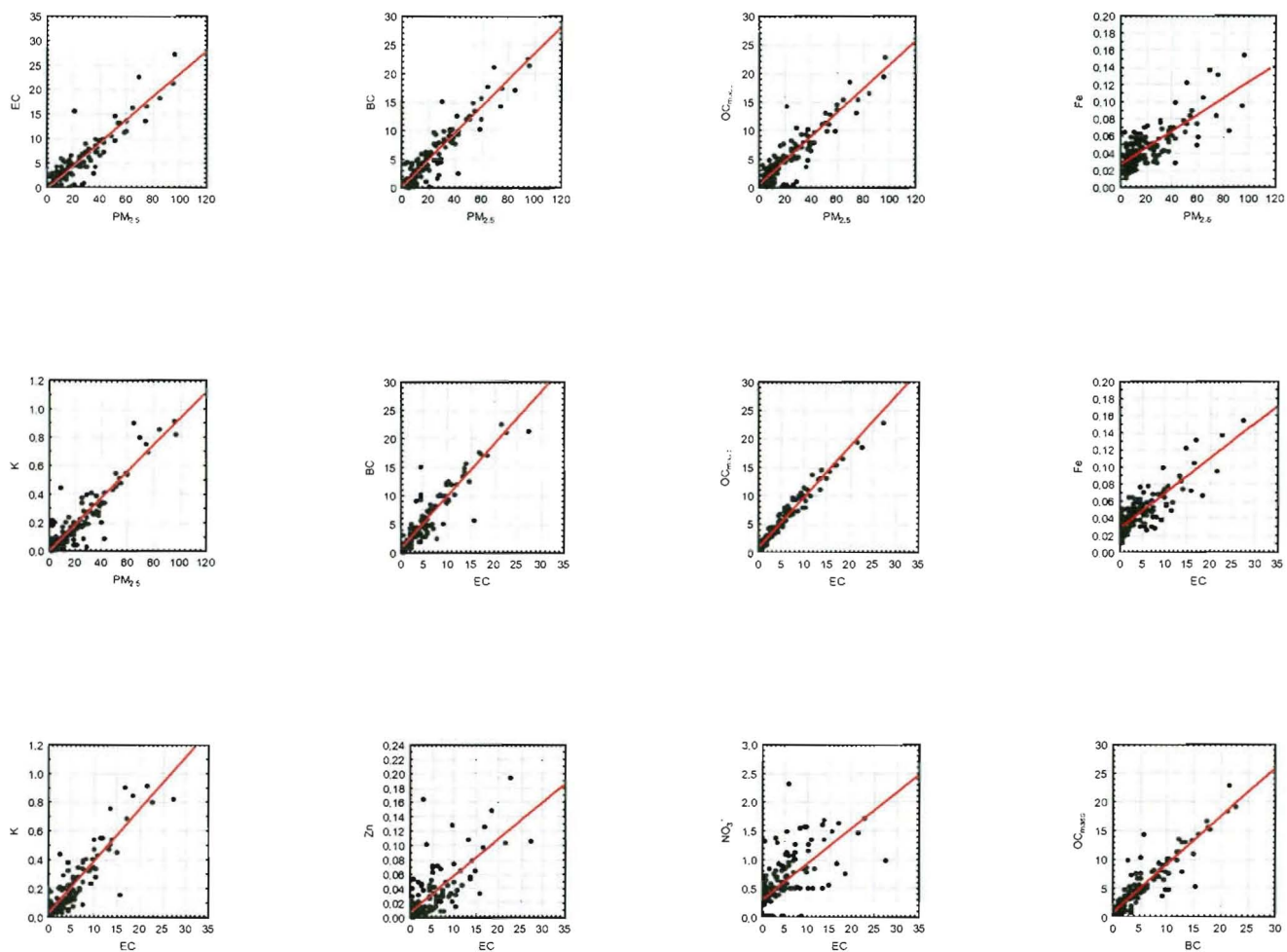


Figure 7.14 Inter-relationships between highly correlated species, Christchurch, 2001/2002.

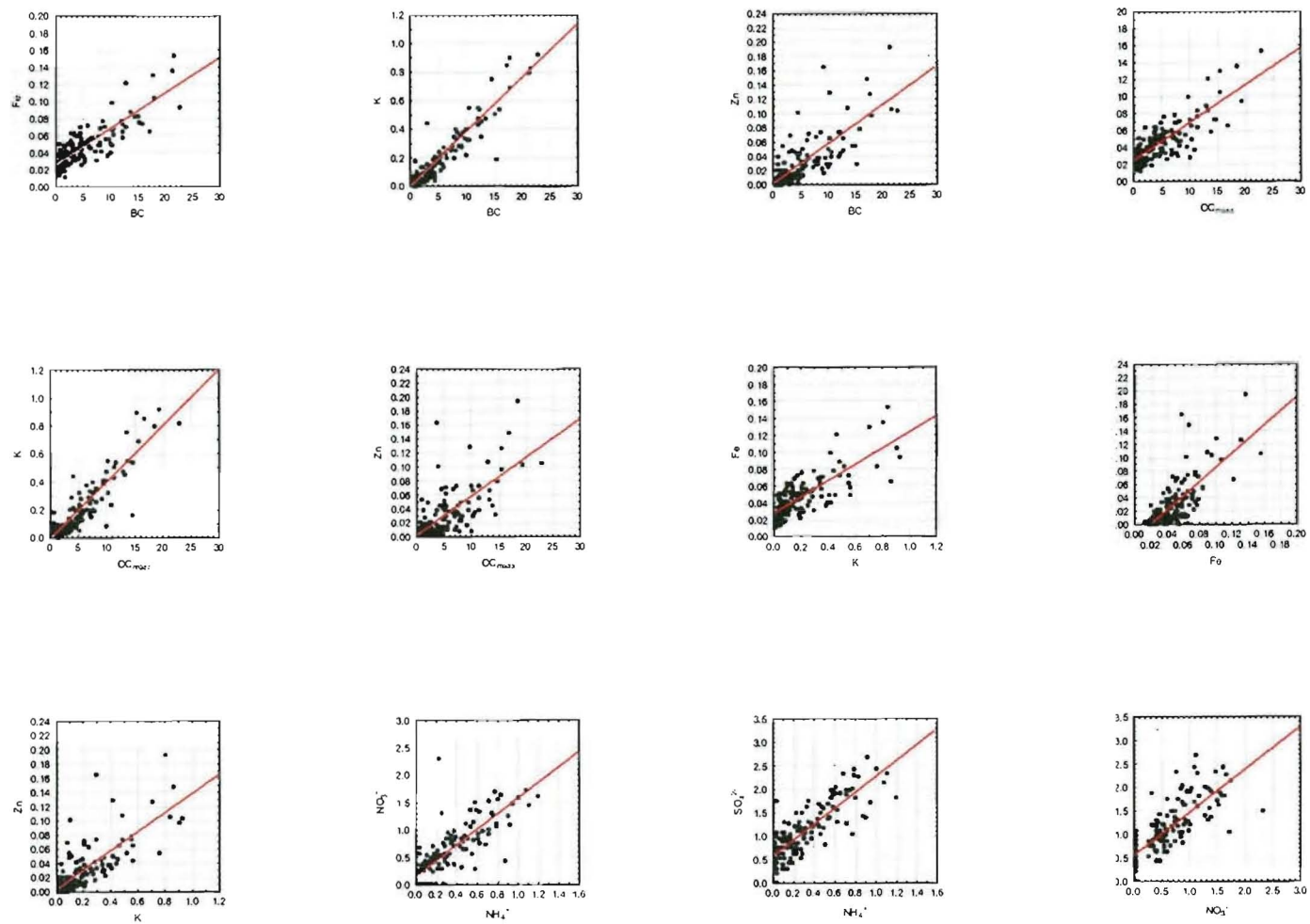


Figure 7.14 continued ..

7.7 Preliminary source identification using Principal Components Analysis

A PCA using Statistica 6.0 software was performed on the combined summer and winter dataset to provide a quick overall assessment of the data. EC and sulphate were excluded from the analysis to prevent double-counting with BC and sulphur. At this stage of the analysis, BC was the primary carbon species used and was supplemented with OC_{mass} (although there were some reservations regarding the representativeness of the measurement).

The PCA assists in determining the number of factors to select for the receptor modelling and provides an initial indication of potential sources. Review of the eigenvalues derived during the analysis (Figure 6.6) suggested a four to eight factor solution was appropriate. After conducting multiple runs and evaluating the factor profiles, a five factor solution was eventually selected. Rotation of the data was required to provide a more realistic distribution of elements in the factor profiles. This was conducted using a varimax raw rotation technique. The source profiles obtained are outlined in Table 7.4. The factor loadings presented represent the strength of correlations between each element and factor (component or contaminant source). Elements with factor loadings greater than 0.7 are highlighted to identify the principal constituents of each factor.

Table 7.4 Factor loadings matrix obtained using PCA, 5 factors, Christchurch, 2001/2002.

Factor loadings (Varimax raw)					
Species	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
S	0.40	0.08	-0.21	0.75	0.17
Cl	0.12	0.89	0.00	-0.19	-0.06
Si	0.43	-0.11	0.07	0.37	0.53
Fe	0.81	0.05	0.14	0.27	0.30
K	0.92	0.11	0.05	0.19	0.11
Mg	0.07	0.61	0.46	0.28	0.30
Na	-0.11	0.87	-0.18	0.01	-0.12
Ca	0.35	0.71	-0.09	0.16	0.19
Zn	0.84	0.00	-0.08	0.24	0.12
Cr	0.14	-0.20	0.78	0.19	-0.01
Ni	0.19	-0.02	0.61	-0.13	0.41
Al	0.22	0.00	0.08	0.07	0.87
NH ₄ ⁺	0.45	-0.11	0.22	0.79	0.03
NO ₃ ⁻	0.48	0.01	0.28	0.70	0.03
BC	0.93	0.06	0.08	0.22	0.09
OC _{mass}	0.91	0.04	0.15	0.20	0.09
Expl.Var	4.93	2.51	1.47	2.26	1.51
Prp.Totl	0.31	0.16	0.09	0.14	0.09

Factor 1 included iron, potassium, zinc, BC and OC_{mass}. These are all key combustion species and this factor most likely represents a combined wood smoke, motor vehicle and industrial combustion source. Factor 2 was more distinct, with chlorine and sodium grouped together, suggesting a marine

aerosol source. Primary elements present in Factors 3 and 5 were chromium and aluminium respectively. It is unknown exactly what these factors represent, but industrial sources are likely. Factor 4 most likely denotes a secondary particulate source with significant species including sulphur, ammonium and nitrate.

Seventy-nine percent of the variance in the dataset was accounted for by the analysis (i.e. all five factors). However, despite rotation, the majority of the variance remained in Factor 1 (31%). The ability of PCA to successfully resolve sources is clearly limited with only two sources sufficiently differentiated from the others; marine aerosol and secondary particulate.

7.8 Preliminary source identification by Positive Matrix Factorisation

The PMF analysis was conducted in accordance with the methodology outlined in Section 6.5.2. Multiple runs were performed to optimise the analysis as determined by a favourable Q-value and realistic factors. The model results presented in this section are preliminary, as the dataset was reanalysed after the OC/EC investigation was completed in 2004.

Initially, meteorological variables like wind speed and direction, and continuous data such as CO, NO_x and SO₂ were included in the analysis. These runs were unsuccessful and the variables were subsequently eliminated from the dataset. Different numbers of factors, ranging from 4 to 10, were also investigated with five factors eventually selected. In addition, separate modelling was conducted on the summer and winter datasets to determine whether seasonal data could improve source resolution. The small size of the datasets, however, limited the ability of the model to provide more than three sensible factors. The summertime factors were identified as marine aerosol, secondary particulate and motor vehicles, and the winter factors as motor vehicles, marine aerosol and wood combustion. Although the summer modelling resolved a better marine aerosol profile (which incorporated sulphur), a weaker marine aerosol profile was resolved in winter, which included substantial quantities of OC_{mass} (35%) and BC (14%). Other known sources including secondary particulate, summertime wood combustion and industry were not resolved. The size of the dataset clearly influenced the number of sources that could be obtained, and while analysis by season provided a reasonable assessment of the predominant sources, it over-simplified the situation in Christchurch. It was concluded that the best overall representation of sources contributing to PM_{2.5} in Christchurch would most likely be obtained by analysing the entire dataset.

The receptor modelling results presented in this chapter were generated from the analysis of the combined summer and winter dataset. Evaluation of the Q-values, residual matrices and source profiles suggested that a five-factor solution was optimal. The Q-value for the five-factor solution (1702) compared favourably to the theoretical Q-value (between 1669 and 2544). The most central solution (f-peak=0) was used, as there was little rotational freedom evident in the G-Factors (i.e.

rotation would force values to become negative). The source profiles obtained by the model were reviewed and subsequently identified.

7.8.1 Source profiles

The F-Factor matrix output by the PMF receptor model produces factor loadings in $\mu\text{g m}^{-3}$ allowing elemental profiles (relative elemental abundances to the elemental sum) to be derived directly. The profiles obtained for the preliminary five factor solution (Table 7.5) are described briefly in this section.

PMF groups elements into factors, but cannot actually name the sources represented by those factors. This is determined by the modeller, and additional information is usually required. The factor profiles obtained by this study were evaluated against other New Zealand based profiles, those published in the international literature and contained in the USEPA's Speciate 3.2 database.⁴¹ The source identification process for the final analysis is discussed in detail in Chapter 10.

Factor 1 was identified as a "wood combustion" source. The most abundant species present were BC (51%) followed by OC_{mass} (45%), potassium (2%), chlorine (1%) and nitrate (1%). Potassium is a widely known marker for wood smoke and its association with carbon compounds is a strong indication that this comprises a wood combustion source (Chan *et al.*, 1997; Maykut *et al.*, 2003; Polissar *et al.*, 1998; Ramadan *et al.*, 2000; Watson *et al.*, 1991). This is confirmed by wood combustion profiles obtained from source testing and receptor modelling studies, that also include these species (Chapter 10).

Factor 2 represents marine aerosol, where almost all species found in sea water are present including chlorine (51%), nitrate (4%), potassium (1%), magnesium (3%), sodium (38%) and calcium (1%). However, sulphur was absent from the profile and small quantities of OC, silicon, iron, BC and nickel were evident. Sulphur was present in two of the other profiles identified, both of which represent photochemical/secondary sources. Therefore, marine aerosol-derived sulphur has most likely been transformed through photochemical processes into a secondary particulate species and thus become associated with other sources. The presence of small quantities of other chemical species in the marine source profile is not a great concern. These may comprise combustion or secondary derived particles that have been transported in the easterly sea breeze, along with marine aerosol, across the city to the receptor site at Coles Place.

⁴¹ The USEPA stores all its source emission profiles in the Speciate 3.2 database. These are used for receptor modelling and emission inventory purposes.

Table 7.5 Factor loadings matrix obtained using PMF, preliminary 5 factor solution, Christchurch, 2001/2002.

	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
S	0.00	0.00	0.35	0.15	0.00
Cl	0.07	0.42	0.00	0.00	0.00
Si	0.01	0.00	0.05	0.00	0.06
Fe	0.01	0.00	0.01	0.00	0.02
K	0.15	0.01	0.02	0.00	0.00
Mg	0.00	0.03	0.04	0.02	0.03
Na	0.00	0.31	0.28	0.00	0.07
Ca	0.00	0.01	0.02	0.00	0.01
Zn	0.02	0.00	0.00	0.00	0.00
Cr	0.00	0.00	0.00	0.00	0.01
Ni	0.00	0.00	0.00	0.00	0.00
Al	0.00	0.00	0.01	0.00	0.01
NH ₄ ⁺	0.00	0.00	0.00	0.29	0.00
NO ₃ ⁻	0.07	0.03	0.00	0.36	0.12
BC	3.77	0.01	0.12	0.18	0.40
OC _{mass}	3.31	0.00	0.00	0.19	0.93
Sum	7.425	0.826	0.903	1.192	1.664
	Wood combustion	Marine aerosol	Aged aerosol	Secondary particulate	Motor vehicles
S		0.1%	38.6%	12.3%	
Cl	1.0%	51.1%	0.1%	0.2%	0.1%
Si	0.1%	0.3%	5.9%	0.1%	3.7%
Fe	0.2%	0.2%	1.2%		1.1%
K	2.0%	0.9%	1.7%		
Mg		3.4%	4.2%	1.4%	2.1%
Na		38.1%	31.2%	0.1%	3.9%
Ca	0.1%	1.3%	1.8%		0.4%
Zn	0.2%		0.3%	0.2%	0.1%
Cr			0.3%		0.3%
Ni		0.1%	0.2%		0.1%
Al			1.4%		0.7%
NH ₄ ⁺				24.6%	
NO ₃ ⁻	1.0%	3.5%		29.9%	7.4%
BC	50.8%	0.8%	12.9%	15.5%	24.2%
OC _{mass}	44.6%	0.3%	0.1%	15.8%	55.8%

Factor 3 contained high quantities of sulphur (39%), sodium (31%) and BC (13%). Initially the high sulphur content led to the indeterminate label of "sulphur source". However, there were many other species present in the profile, including silicon (6%), iron (1%), potassium (2%), magnesium (4%), calcium (2%) and aluminium (1%). The presence of carbon, soil related species and metals also suggested a diesel-vehicle or industrial fuel-oil source. Investigation of the proportion of carbon to sulphur, where sulphur is substantially more abundant relative to BC, did not support this. Review of

the literature subsequently found that sources with similar sodium and sulphur-dominated profiles have been identified elsewhere. These were labelled long-range transport or aged marine aerosol sources. The relative abundance of sodium and sulphur suggests that Na_2SO_4 may be present, and if so, that this factor potentially represented an aged (photochemical) source.

A secondary particulate source (Factor 4) was also resolved by the modelling. This was characterised by the presence of secondary particulate species including ammonium (25%) and nitrate (30%). Sulphur was abundant (12%) and likely to be in the form of sulphate. OC_{mass} , which is present in primary and secondary forms, was also a significant elemental constituent (16%), as was BC (16%). Nitrates and sulphates are formed from anthropogenic combustion (including motor vehicles) and natural emissions, and secondary organic compounds may be derived from wood smoke.

Factor 5 was identified as a motor vehicle source due to the presence of combustion-related species including OC and BC (56% and 24% respectively), secondary species such as nitrate (7%), soil related elements including silicon (4%), iron (1%), calcium (0.4%) and aluminium (1%), and metals such as zinc (0.1%), nickel (0.1%) and chromium (0.3%). These species are commonly found in emissions from engine combustion, and from the re-entrainment of road-dust and wear-and-tear of brake pads. Species such as sodium and magnesium, however, are more likely to be associated with marine aerosol than motor vehicles. Nevertheless, only minimal amounts were detected in the motor vehicle profile and it may be that uncertainties associated with low concentrations of these elements were not sufficiently allocated.

There were a number of contaminant sources in Christchurch not resolved by the model. These included industry, coal burning, soil and diesel vehicles. It was probable that these sources were incorporated into the other source profiles. Sulphur and heavy metals in the motor vehicle and aged aerosol profiles, for example, were also likely to be associated with industry, coal burning and diesel. Soil, while not existing as a factor in its own right, also appeared to be split between these two profiles, with elements such as silicon, iron and calcium present in both profiles. While it is disappointing these sources were not resolved separately, emission inventory data suggests that emissions from sources such as industry may be relatively insignificant in the Inner Christchurch area (Scott and Gunatilaka, 2004).

Overall, these profiles were considered to be reasonable representations of the sources concerned. However, the relative abundance of OC_{mass} (45%) to BC (51%) in the profile identified as wood combustion was a concern. Normally, emissions from low temperature wood combustion sources have a greater abundance of OC_{mass} to EC. In residential wood combustion profiles found in the USEPA's Speciate 3.2 database, for example, abundances of 42 to 48% for OC and 10 to 15% for EC are indicated. This anomaly, whilst most likely associated with the OC/EC measurement issues discussed in the following chapter, could potentially lead to misinterpretation of the factors resolved

by the modelling. To address these concerns, a dedicated study of OC and EC was conducted in Christchurch during the winter of 2004 (Chapter 8). It found that OC_{mass} measures were underestimated during 2001/2002. The dataset was subsequently revised and the analysis repeated. The final modelling and source apportionment results are presented in detail in Chapter 9.

7.9 Summary

Speciated $PM_{2.5}$ measurements were conducted during the summer of 2001/2002, and the winter of 2002. The major chemical constituents of summertime $PM_{2.5}$ were OC_{mass} , BC, EC, sulphate, sodium, chlorine and sulphur. Similar species dominated in the winter, along with nitrate. Most elemental species, with the exception of sulphur and the major constituents of marine aerosol (e.g. sodium and chlorine), were more abundant during the winter months. Seasonal variations in emissions (especially for potassium), and meteorological conditions, were primary contributing factors.

A Spearman R correlation analysis was undertaken to provide an initial indication of potential elemental groupings and sources. The strongest correlations were between the carbon compounds, iron, potassium and zinc, and between the secondary particulate species. When the relationships were assessed on a seasonal basis, the greatest associations were between the constituents of marine aerosol (i.e. sodium, chlorine, calcium and magnesium) in summer, and between the combustion and secondary particulate species in winter.

A PCA analysis was conducted on the entire summer and wintertime dataset to determine possible factor numbers and source types. The majority of the data variance was accounted for in the first factor, and only two sources were sufficiently resolved from the others (marine aerosol and secondary particulate). The data were reanalysed using the PMF receptor model. Five factors were resolved including motor vehicles, marine aerosol, wood combustion, secondary particulate and aged aerosol. However, issues associated with the OC and EC measurements led to an additional investigation of OC and EC during the winter of 2004 (Chapter 8). Subsequently, the PMF analysis was revised and the final results are presented in Chapter 9.

Chapter 8: Organic and elemental carbon study

8.1 Introduction

The carbon species measured during this study were OC, EC and BC. OC and EC concentrations were measured continuously using an R&P Series 5400 analyser, and BC by light reflection/transmission. Statistical summaries of the data are presented in Chapter 7. While conducting the data analysis, it became evident that the concentrations measured were atypical to those observed elsewhere (e.g. Ito *et al.*, 2004; Chow *et al.*, 1993). The OC and EC data were highly correlated, of similar magnitudes, and in some instances, EC concentrations were greater than OC. Subsequent investigation of the monitoring records revealed that the temperature setting used by the Series 5400 during the study to differentiate between OC and EC (230°C) was different to that recommended by the instrument manufacturer (340°C). This could potentially lead to an underestimate of OC and an overestimate of EC, relative to measurements elsewhere.⁴² OC and EC measures are operationally defined, and ideally, comparisons should only be made with those studies where the same, or equivalent, analytical methods are used. This limits the usefulness of the concentrations reported by this study as no studies outside Christchurch could be found, where a differentiation temperature of 230°C was used.

In this regard, preference was given to using the BC measurements, rather than EC, in the receptor modelling. As it was critical for a high proportion of the PM_{2.5} mass to be explained by the chemical species measured, the Series 5400 OC concentrations (as OC_{mass}) were also included in the modelling. It was accepted that this could potentially lead to an underestimate of the source contributions. The PMF receptor model was subsequently applied to the data and five sources were resolved including wood combustion, motor vehicles, marine aerosol, aged aerosol and secondary particulate (Section 7.8). Although the factors were readily identified, there were some concerns about the distribution of OC_{mass} and BC in the source profiles. The relative abundance of OC_{mass} (45%) to BC (51%) in the factor identified as wood combustion was contrary to that normally expected, where low temperature combustion sources such as residential wood burning appliances typically discharge more OC than EC. Therefore, not only could including OC_{mass} as a separate chemical species in the receptor modelling result in an underestimate of the source contributions, but could also lead to misinterpretation of the resolved factors. Further investigation of OC and EC concentrations in Christchurch was warranted on this basis.

⁴² That is, at a lower temperature setting a lesser proportion of TC will be attributed to OC and a greater proportion to EC, than when a higher temperature setting is used. Assuming that the Series 5400 was designed to produce data comparable to more widely accepted methods such as TOR, it is probable that a lower combustion temperature would also provide proportionately lower OC estimates to those indicated by other methods.

In response to these concerns, additional work was conducted to confirm the representativeness of the 2001/2002 measurements and to provide data that may be more readily compared with other source apportionment or chemical composition studies. A dedicated study of OC and EC was undertaken during the winter of 2004 and concentrations determined using co-located filter-based and continuous methods. Quartz-fibre filters were analysed using the widely accepted and used thermal/optical reflectance technique (TOR), and the data evaluated against continuous measurements provided by the Series 5400. The continuous analyser was set at the same non-default temperature setting as that used in 2001/2002, to determine variations in results between analytical methods. This chapter presents the OC and EC concentrations measured during the 2004 study, compares the two measurement/analytical methods, and discusses the implications of these findings for the wider study.

8.2 Background

This section describes the key characteristics of OC and EC including potential impacts on the environment, use in source identification and outlines issues associated with the OC and EC measurements. These factors highlight the need for an improved knowledge and understanding of these important atmospheric contaminants. This is particularly relevant for Christchurch where $PM_{2.5}$ is often elevated during the winter months, and OC and EC are the key chemical constituents. If concentrations of OC and EC are reduced, similar declines in $PM_{2.5}$ are likely. Robust measurements of OC and EC are therefore required. Issues associated with the 2001/2002 measurements are discussed in more detail to provide the basis for undertaking this additional work.

8.2.1 Overview of OC and EC

Abundance in fine particles

OC and EC are the most abundant chemical species present in $PM_{2.5}$ in urban environments. The contribution of carbon compounds to $PM_{2.5}$ mass varies by location with average contributions of 44% for Vienna (Austria), 40% for Los Angeles (USA), 50% for many Canadian cities, 48% for Montana (USA) and between 40 to 60% at various locations in California (Salam *et al.*, unpublished; Bennett and Stockburger, 1994; Brook and Dann, 1999; Ward *et al.*, 2004; Chow *et al.*, 1996b). OC alone can constitute up to 10 to 70% of $PM_{2.5}$ (Turpin *et al.*, 2000). These contributions vary by season and by the measurement method used.

The measurements conducted during 2001/2002 suggest that OC and EC are the key chemical constituents of $PM_{2.5}$ in Christchurch. As indicated in Chapter 7, the concentrations of EC ranged from 0.2 to 27 $\mu g m^{-3}$, OC_{mass} from 0.4 to 23 $\mu g m^{-3}$ and BC from 0.2 to 23 $\mu g m^{-3}$. The maximum EC and OC_{mass} concentrations occurred on 22 May 2002 and contributed to 28% and 24% of $PM_{2.5}$, respectively, with a total contribution of 52%. The maximum BC concentration occurred on 9 July 2002 and contributed to 24% of the fine particle mass. On high $PM_{2.5}$ days (i.e. $>25 \mu g m^{-3}$) OC and EC contributed on average to 34% of $PM_{2.5}$, with daily contributions ranging from 5% to 68%.

Impacts associated with OC and EC

Section 2.2.1 describes the formation of, and the compounds present in, EC and OC. OC is of particular concern as it comprises an aggregate of hundreds of individual compounds, some of which are known human carcinogens. This poses a potential health issue in Christchurch, as OC is likely to constitute a significant proportion of fine particle mass. A study conducted by Krivácsy *et al.* (2005) found organic species, including a range of carbohydrate derivatives, substituted benzenes and toluenes, resin acids, aromatic acids, dicarboxylic acids, humic-like substances and fatty acids were present in atmospheric particles in Christchurch. Organic compounds such as these are usually present in the PM_{2.5} fraction and may be readily transferred into the human respiratory system.

While potential health effects are the main concern, OC and EC also have significant impacts on visibility and climate change. OC scatters incoming radiation back into space while EC absorbs incoming light. Light scattering has two effects - it reduces visibility, and potentially results in negative climate forcing (cooling effect) by radiating energy away from the Earth's surface (Seinfeld and Pandis, 1998). The impact of OC on light scattering and visibility is of a similar magnitude to that of other visibility degradation species such as sulphates (Cachier, 1998; Turpin *et al.*, 2000). Light absorption (by EC) can also result in visibility degradation, potentially leads to positive climate forcing (heating effect), and contributes to global warming (Horvath, 1993; Jacobson, 2001; Yu *et al.*, 2004; Seinfeld and Pandis, 1998). EC also acts as a catalyst and can interfere with important atmospheric chemical reactions (Cao *et al.*, 2004; Bennett and Stockburger, 1994). The ability of OC and EC to influence the properties and nucleating ability of cloud condensation nuclei can also contribute to global climate change (Lim *et al.*, 2003). The number of cloud condensation nuclei affects cloud cover, cloud optical properties and precipitation ability (Cachier, 1998). Cachier (1998) also suggests that fresh biomass burning aerosols have a more active influence on cloud condensation nuclei than industrially derived particles.

Fortunately, as OC is mainly comprised of water-soluble species, it is readily removed from the atmosphere. Typical residence times range from 4 to 5 days. EC, conversely, remains longer in the atmosphere with estimated residence times of 4 to 10 days (Lim *et al.*, 2003; Höller *et al.*, 2002).

Use of OC and EC in source identification

Primary OC and EC are produced during the combustion of fossil fuels from industrial processes, biomass burning (including residential heating and outdoor burning), and motor vehicles. Sources such as residential heating and petrol-fuelled vehicles produce relatively high quantities of OC relative to EC, whereas diesel vehicles and some industries discharge higher quantities of EC. OC is also produced through secondary reactions, where organic gases condense into fine particles. Biogenic sources of organics include vegetation, plant waxes and pollens (Seinfeld and Pandis, 1998).

The proportional abundance of OC and EC (or OC and Total Carbon (TC)) is often used to identify factors derived from receptor modelling. Chow and Watson (1998), for example, reported OC/TC ratios of 0.58 for motor vehicles in northwestern Colorado, and ratios of 0.69 for petrol-fuelled vehicles, 0.55 for diesel-fuelled vehicles and 0.52 for mixed vehicle fuel types from other studies. The OC/TC ratios quoted for residential wood combustion were 0.73 and 0.81. However, a ratio approach for source apportionment purposes can be problematic, as several studies have noted substantial variations in the data, even from sources within a single category. Cabada *et al.* (2002) indicated that EC from wood burning profiles presented in the literature varied in accordance with the nature of the wood consumed and the characteristics of combustion. Watson *et al.* (1994) also reported that species discharged from motor vehicles were highly variable and dependent on the vehicle, fuel used and operating mode. While caution is advised regarding the use of OC and EC ratios for source identification purposes, the breakdown of these compounds into additional temperature-dependent carbon fractions (such as those provided by the TOR method) has proved useful (Watson *et al.*, 1994; Lowenthal and Rahn, 1987). Kim and Hopke (2003) found TOR measurements (provided at different temperature steps) allowed factors to be resolved separately for petrol- and diesel-fuelled vehicles.

OC and EC ratios may also be used to determine the significance of secondary organics in a particular area. Studies such as Chow *et al.* (1993; 1996), Cao *et al.* (2004) and Lee *et al.* (2002a,b) suggest that an OC/EC ratio >2 is indicative of secondary organics. However, as Yu *et al.* (2004) pointed out, the ratio of OC/EC is a function of the emission sources contributing to the measured concentrations and other measures should be used in conjunction with the ratios to determine the secondary OC component.

Measurement of OC and EC

The sampling and analysis of OC and EC is complicated and challenging. Issues associated with the measurement of these chemical compounds are outlined in Turpin *et al.* (2000) and Bennett and Stockburger (1994). The measurements obtained are operationally defined, and the method of analysis and key analytical parameters must be reported together with the OC and EC concentrations. Comparisons with other measurements should ideally only be conducted with concentrations determined using the same or equivalent methodologies.

Key to the measurement issue is the semi-volatile nature of organic compounds, which continuously transfer between the gas and particle phases. This is especially problematic for filter-based sampling, where organics present on a filter can volatilise resulting in lower mass (negative artifact) or organic vapours adsorbing onto the filter surface leading to higher mass measurements (positive artifact). This is further exacerbated by the sampler configuration and analytical environments used, which can vary the amount of volatilisation and adsorption by as much as 50 to 60% (Huebert and Charlson, 2000). Consequently, the filter media, instrumentation and analytical methods used to measure OC and EC are vital considerations for any carbon study. Ten Brink *et al.* (2004) conducted an

intercomparison study of different methods and found OC concentrations varied by greater than a factor of two. While there were large absolute differences between samplers, on a proportional basis, the amounts of EC were similar.

A variety of collection systems may be used to sample for carbon compounds including impactors or filter-based systems. The literature suggests that quartz-fibre is the most appropriate medium for carbon sampling and analysis (Lee and Kang, 2001; Chow and Watson, 1998; Turpin *et al.*, 2000). However, quartz-fibre filters adsorb some organic vapours during sampling, which must be eliminated from the measurement. Parallel port systems or denuders are recommended to avoid, or correct for, organic vapour adsorption. The preferred option is to use a denuder to remove the gas-phase organics. Denuders contain an adsorbent surface such as activated carbon and as the sample passes through the denuder, gas-phase organics diffuse onto its surface and the remaining sample is then deposited onto a filter.

There are a variety of analytical methods used to measure OC, EC and individual organic compounds. These include thermal methods, filter extraction and analysis by gas chromatography-mass spectroscopy, and organic tracer and isotope analysis. Thermal techniques are more commonly used as these are relatively simple to conduct and are cost-effective (Turpin *et al.*, 2000). There are at least 15 thermal combustion methods available internationally (Chow, 2003). Differences between methods include combustion atmospheres, temperature ramping rates and times, sample aliquot and size, oxidation catalysts, evolved carbon detection methods, carrier gases, and monitoring configuration. Popular thermal methods include continuous measurements from analysers such as the R&P Series 5400, and analysis of quartz-fibre filters by thermal manganese dioxide oxidation (TMO), TOR, or thermal optical transmittance (TOT). The thermal method employed by the Series 5400 differs from the filter-based methods in that oxygen is present throughout the analysis, and OC and EC are determined by the combustion temperatures used.

Estimation of organic mass

Current analytical methods used to measure OC provide a measure of the mass of carbon in organics rather than the mass of the actual organic compounds (Turpin *et al.*, 2000). Other elemental species associated with organic mass such as oxygen, hydrogen and nitrogen are not included in the measurement and need to be estimated using factors suggested in the literature. These factors which represent the average organic molecular weight per carbon weight can vary substantially with the most common values ranging from 1.2 to 1.6 (Brook and Dann, 1999; Chow *et al.*, 1994; Turpin *et al.*, 1997; Salma *et al.*, 2004; Salam *et al.*, unpublished). Turpin and Lim (2001) investigated the accuracy of these factors, and in particular, the most frequently used value of 1.4. They found that conversion values of 1.6 and 2.1 more accurately described the average molecular weight per carbon weight for "urban" and "aged (non-urban)" aerosols. Further, it was suggested that values of 2.2 to 2.6 better represented aerosol heavily impacted by wood smoke. The value of 1.4 may be

appropriate for fresh emissions, but a higher multiplier might be applicable for emissions that have had some time to oxidise (Robinson *et al.*, 2004). Consequently, measures of OC_{mass} can vary and may be under- or over-estimated depending on the actual conversion factor used and the nature of the air quality environment. A value of 1.4 was applied to the 2001/2002 OC measurements. However, a higher conversion value may have been more appropriate.

8.2.2 Issues associated with the 2001/2002 OC and EC measurements

As part of the validation and analytical process, all chemical species measured during 2001/2002 study were plotted against each other. This provided an indication of species relationships and the presence of any anomalous data. Issues with OC and EC were flagged at this stage, owing to the high degree of correlation between the two species (r^2 value of 0.96; Figure 8.1). This suggested that the species were derived from a single source, or that meteorology had an equal impact on all OC and EC sources, or that a potential data issue existed.

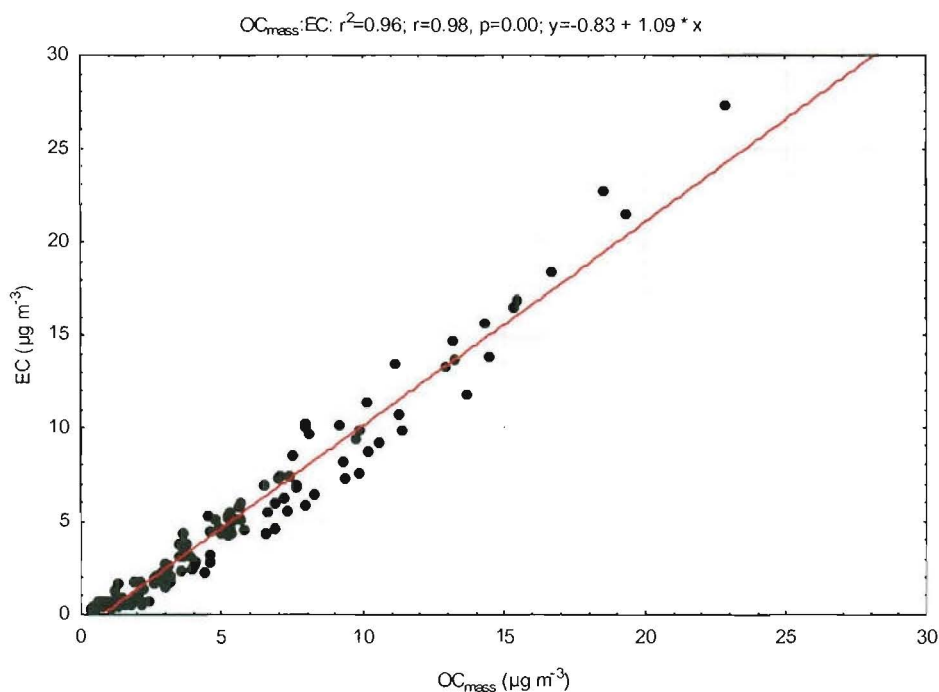


Figure 8.1 Relationship between 24-hour average OC_{mass} and EC concentrations measured by the Series 5400, Christchurch, 2001/2002.

Figure 8.1 also shows that the EC concentrations in Christchurch were of a similar magnitude to, or were more abundant than OC_{mass} . To determine whether this was typical, the data were evaluated against concentrations observed elsewhere. Although actual OC and EC concentrations measured using one method should not be compared with those collected and analysed by another method, a comparison that focuses on the relativities of the species is useful for highlighting potential measurement issues.

Table 8.1 presents a statistical summary of the 2001/2002 Series 5400 data together with BC measurements obtained by light reflection using a M43D digital smoke stain reflectometer. Greater detail on these measurements is provided in Chapter 7. When the OC_{mass} measurements are converted back to OC, the total OC mean is $3.2 \mu\text{g m}^{-3}$, the total maximum is $16.4 \mu\text{g m}^{-3}$, the summer mean is $0.7 \mu\text{g m}^{-3}$, the summer maximum is $1.7 \mu\text{g m}^{-3}$, the winter mean is $5 \mu\text{g m}^{-3}$ and the winter maximum is $16.4 \mu\text{g m}^{-3}$.

Table 8.1 Statistical summary of 24-hour average $PM_{2.5}$ carbon measurements ($\mu\text{g m}^{-3}$), Christchurch, 2001/2002.

All data	Mean	Valid N	Median	Minimum	Maximum	25th percentile	75th percentile	Standard deviation
BC	4.6	159	2.9	0.15	22.7	1.1	6.3	4.8
OC_{mass}	4.5 (3.2)	159	3.2	0.38	22.9 (16.4)	1.1	6.7	4.4
EC	4.1	159	2.3	0.22	27.3	0.5	5.7	4.9
Summer	Mean	Valid N	Median	Minimum	Maximum	25th percentile	75th percentile	Standard deviation
BC	1.1	65	0.9	0.2	3.4	0.6	1.3	0.6
OC_{mass}	1.0 (0.7)	65	0.9	0.4	2.4 (1.7)	0.7	1.2	0.5
EC	0.5	65	0.5	0.2	1.7	0.4	0.6	0.3
Winter	Mean	Valid N	Median	Minimum	Maximum	25th percentile	75th percentile	Standard deviation
BC	7.0	94	5.2	0.8	22.7	3.2	9.8	5.0
OC_{mass}	7.0 (5.0)	94	5.4	2.0	22.9 (16.4)	3.7	9.1	4.3
EC	6.6	94	5.1	1.1	27.3	3.1	8.7	5.1

NB: The values in brackets are unconverted OC_{mass} measurements.

Table 8.2 presents OC and EC data from eight different studies using a variety of analytical methods. A comparison of the Christchurch measurements with those indicated in the "Total" column of Table 8.2 found that the OC mean concentrations were of similar magnitudes, whereas the Christchurch EC and BC means were higher than many of the overseas measurements. Maximum OC was lower than those detected in Seattle, USA, and Chongju, Korea, while maximum EC and BC were substantially higher in Christchurch. Although, this may simply be a reflection of differences associated with the analytical methodologies, in most of the studies listed in Table 8.2, OC was present at higher concentrations than EC. As the ratio of OC to EC can be indicative of source origin, the Christchurch data would appear to suggest the presence of a source or sources that discharge high quantities of EC relative to OC. Alternatively, and more likely, the Series 5400 (@ 230°C) was not providing OC and EC data equivalent to the filter-based methods (i.e. the species were incorrectly differentiated). As previously mentioned, subsequent investigation of the monitoring records revealed that a non-default temperature setting (230°C) had been used to distinguish between OC and EC in 2001/2002. While the impact of this difference on the concentrations of the two carbon fractions was uncertain, it was likely that the OC concentrations were being underestimated.

Table 8.2 Summary of 24-hour average PM_{2.5} OC and EC measurements ($\mu\text{g m}^{-3}$) from a variety of international studies.

Study	Method, location & sample size	Summer				Winter				Total			
		Mean		Maximum		Mean		Maximum		Mean		Maximum	
		OC	EC	OC	EC	OC	EC	OC	EC	OC	EC	OC	EC
Ito <i>et al.</i> (2004)	Thermal optical analysis, New York, USA, 189,170,171									5.0 4.0 3.7	1.3 1.1 0.7		
Maykut <i>et al.</i> (2003)	TOR, Seattle, USA 289									2.9	1.1	18.9	6.2
Hansen <i>et al.</i> (2003)	TOR, Pensacola & Gulfport, Mexico, not stated									3.7 3.1	1.1 0.83		
Brook and Dann (1999) - medians presented	TOR, Vancouver and Toronto, Canada, 28, 85, 26, 82, 24									2.2 2.1 2.3 2.1 4.5	0.6 0.9 0.6 0.9 4.5		
Chow <i>et al.</i> (1993)	TOR, San Joaquin Valley, USA, 35, 33, 35, 35, 35, 33									5.4 3.3 8.1 2.7 3.3 6.5	3.9 1.5 6.7 1.2 1.1 5.4		
Chow <i>et al.</i> (1994) - samples collected in autumn rather than winter	TMO, Southern California, USA, 5 sites (including downtown Los Angeles), 11 samples each	9.1 8.3 3.4 3.4 4.7	2.2 2.4 0.7 1 1.2	11 10.8 5.3 6.3 7.3	3.4 5.4 1.9 3.1 3.4	19.6 18.5 14 17.8 13.9	6.3 7.3 5.8 6 5.5	31 27.8 22.7 33.2 20.7	9 12.1 7.8 9.0 8.6				
Park <i>et al.</i> (2001)	TMO, Sihwa, Korea, 53									9.9	1.8		
Lee and Kang (2001)	TOR, Chongju, South Korea, 15 (winter), 13 (summer), 58 (total)	4.0	3.4	7.4	6.4	5	4.3	9.7	9.9	5	4.4	12.7	12.5

The measurement issues also created difficulties for the receptor modelling, specifically with regard to which carbon species to include. For receptor modelling to be effective, most PM_{2.5} constituents must be included, otherwise the modelling is only representative of a small proportion of the data (Chapter 11). When the Series 5400 OC and EC were used in the modelling, the strong correlation between the measurements of these species led to OC and EC being exclusively resolved into a single factor. However, this was unlikely to represent a valid source as most combustion sources discharge contaminants additional to OC and EC, and other factors would also be expected to have some OC and EC component. Therefore, BC (which was more variable than EC) was selected as the primary carbon species for the modelling, and was supplemented by OC_{mass}. It was accepted that OC_{mass} was probably underestimated, and that additional work would need to be conducted to confirm whether or not this was the case.

Nevertheless, the PMF receptor model was applied to the data and five preliminary sources were resolved. These included motor vehicles, wood combustion, marine aerosol, secondary particulate and aged aerosol (Chapter 7). While the factors were readily identified and considered to be good representations of the sources concerned, there were some issues regarding the relative abundances of OC_{mass} and BC in one of the source profiles. The wood combustion profile, which was primarily comprised of BC (51%), OC_{mass} (45%), potassium (2%), chlorine (1%) and nitrate (1%), had a lower proportion of OC_{mass} to EC than that normally expected for a wood smoke source. The USEPA's Speciate 3.2 database, for example, indicates abundances of 42 to 48% for OC and 10 to 15% for EC, for residential heating emissions.

In response to these measurement and source resolution concerns, a dedicated, short-term OC and EC study was conducted in Christchurch during the winter of 2004.

8.3 Study methodology

8.3.1 Objectives

The 2004 OC and EC study aimed to provide more robust wintertime OC and EC measurements for Christchurch, and to compare data provided by the Series 5400 to those measured using a filter-based technique (TOR). The OC and EC measurements derived are presented for both analytical techniques and the measurement equivalency of the methods discussed.

8.3.2 Site location and instrumentation

Sampling was conducted at Environment Canterbury's Coles Place residential monitoring site from 10 June to 28 July 2004. Two instruments were used to simultaneously collect fine particles for OC and EC analysis. An R&P Series 5400 analyser provided continuous measurement, while a Met One SuperSASS collected samples on 47mm, pre-fired, acceptance-tested quartz-fibre filters. These filters, while being the most suitable medium available for carbon analysis, adsorb organic vapours during sampling. This must be corrected for, or removed from the sample using a denuder. MetOne was unable to supply a denuder for carbon collection so a dual sampling method, such as that suggested in Turpin *et al.* (2000), was adopted. Two canisters were used to determine the final, artifact-corrected OC and EC measurements. The first canister contained a quartz-fibre filter to provide the main uncorrected measurements, and the second canister contained a Teflon/quartz filter in tandem to provide the carbon correction factors. The Teflon filter removes all particulate-phase carbon compounds from the sample and any carbon measured on the quartz back-up filter is assumed to arise from adsorbed gas-phase organics. This measurement is subtracted from the initial quartz filter to provide a final, adjusted OC and EC measurement.

Sampling was conducted at different times, and the Series 5400 analyser set to various temperatures, to determine the impact of the settings on measured concentrations (relative to the filter-based TOR

measurements). The range of sampling times and temperatures investigated are set out in Table 8.3. Measurement equivalency will only be assessed for those days when the Series 5400 was set to 230°C ($n = 21$). All 24-hour average TOR measurements (09:00 to 09:00) will be presented ($n = 20$) to provide an indication of OC and EC concentrations in Christchurch.

Table 8.3 Sampling regime, Christchurch, winter 2004.

Time of day	Number of samples	Series 5400 OC/EC temperature settings
06:00 – 12:00	4	3 @ 230-750 1@ 340-750
12:00 – 18:00	4	3 @ 230-750 1@ 340-750
18:00 – 00:00	3	230-750
00:00 – 06:00	3	230-750
09:00 – 09:00	20	9 @ 230-750 4@ 340-750 6@ 275-750

8.3.3 Analytical methods

As described previously, the Series 5400 employs a thermal CO₂ technique to provide continuous OC and EC measurements. Samples are collected by impaction onto one of two collector plates. Air is transferred from one plate to the other to allow semi-continuous sampling and analysis. The ambient sample is heated, the carbon in the sample volatilises and CO₂ is released and measured. CO₂ is measured prior to analysis to establish a baseline and the collector temperatures are raised to 230°C for a period of eight minutes to oxidise the organic compounds. The temperature is then increased up to 750°C for three minutes to oxidise the remaining carbon. The different carbon species in this instance are defined thermally where all CO₂ produced at 230°C (rather than the default temperature setting of 340°C) is attributed to OC and between 230°C and 750°C to EC. The sum of OC and EC provides a measure of TC.

The quartz-fibre filters were refrigerated and transported to the Desert Research Institute (DRI) located in the US for analysis using the TOR technique (DRI, 2000). A small sample punch is taken from each filter and inserted into a carbon analyser. The sample is then heated incrementally in a helium environment up to a temperature of 650°C. CO₂ generated at 120°C, 250°C, 450°C and 550°C are attributed to OC. The sample is cooled, oxygen is introduced and the temperatures are gradually increased up to 750 or 800°C. CO₂ generated under these conditions is attributed to EC. Pyrolysis of OC, which occurs during the analysis, is corrected for by measuring changes in sample reflectance. The sum of the different OC and EC fractions constitute TC.

8.3.4 Statistical analysis

The TOR measurements comprised a number of OC and EC fractions measured at different temperature steps. The OC concentrations were derived by calculating the sum of OC1, OC2, OC3, OC4 and the pyrolysed component (OP), and EC concentrations by adding EC1, EC2 and EC3 and subtracting OP. Organic adsorption was corrected for by subtracting the back-up quartz-fibre filter measurements from the front quartz filter. The data were entered into a spreadsheet and validated on the basis of the instrument flow rates. Statistica 6.0 was used to prepare statistical summaries of the data, and to compare methods using scatter plots and a Spearman Rank correlation analysis. This was supplemented with a Wilcoxon matched pairs test to determine the significance of the difference between measurement methods.

8.4 Results and discussion

The results for the filter-based TOR measurements are presented as TOR OC, TOR EC and TOR TC with some TOR OC_{mass} results also presented.⁴³ The Series 5400 data are identified as OC_5400, EC_5400 and TC_5400 for OC, EC and TC, respectively.

8.4.1 OC and EC concentrations

Table 8.4 presents summary statistics for 24-hour average OC, EC and PM_{2.5} measured during June and July 2004. The top half of the table is limited to 24-hour TOR measurements and the bottom half to days when the Series 5400 was set at 230°C.

Table 8.4 Summary statistics ($\mu\text{g m}^{-3}$), various measurement periods, Christchurch, winter 2004.

TOR measurements (24-hr averages)	Mean	Valid N	Median	Minimum	Maximum	25th percentile	75th percentile	Standard deviation
TOR OC	19.8	20	12.3	0.6	76.9	7.4	29.4	18.4
TOR EC	5.3	20	4.8	0.5	21.0	3.1	6.0	4.3
TOR TC	25.1	20	17.0	1.1	97.8	10.8	35.0	22.5
PM _{2.5}	43.6	13	37.5	6.4	145.8	17.9	55.7	38.0
TOR & Series 5400 @ 230°C (24-hr averages)	Mean	Valid N	Median	Minimum	Maximum	25th percentile	75th percentile	Standard deviation
TOR OC	19.4	9	23.9	1.9	40.1	3.7	29.4	15.6
OC_5400	9.9	9	12.7	2.3	17.8	5.5	14.3	5.9
TOR EC	5.6	9	5.9	0.7	16.4	1.9	6.3	5.1
EC_5400	7.3	9	9.2	1.2	13.8	2.6	11.3	5.0
TOR TC	25.0	9	31.8	2.6	56.5	5.8	35.4	20.0
TC_5400	17.2	9	21.9	3.6	31.6	8.4	25.4	10.8
PM _{2.5}	40.1	9	44.3	17.1	63.1	21.6	57.0	19.3

During this peak wintertime period, more than 50% of the PM_{2.5} data exceeded the MfE's suggested PM_{2.5} monitoring value of 25 $\mu\text{g m}^{-3}$. The maximum PM_{2.5} concentration (145.8 $\mu\text{g m}^{-3}$), which

⁴³ TOR OC_{mass} = TOR OC x 1.4 to account for other elemental species present in organic compounds.

occurred on 20 July 2004, was almost six times greater than the MfE monitoring value. The TOR TC concentrations ranged from $1.1 \mu\text{g m}^{-3}$ to $97.8 \mu\text{g m}^{-3}$, with a median of $17 \mu\text{g m}^{-3}$ and a 75th percentile concentration of $35 \mu\text{g m}^{-3}$ (24-hour averages). The most abundant species present was OC, which ranged from $0.6 \mu\text{g m}^{-3}$ to $76.9 \mu\text{g m}^{-3}$, with a median of $12.3 \mu\text{g m}^{-3}$ and a 75th percentile concentration of $29.4 \mu\text{g m}^{-3}$. EC ranged from $0.5 \mu\text{g m}^{-3}$ to $21 \mu\text{g m}^{-3}$, with a median of $4.8 \mu\text{g m}^{-3}$ and a 75th percentile concentration of $6 \mu\text{g m}^{-3}$. The TOR means were similar to those measured in autumn in California (Table 8.2) but maximum OC and EC were much higher in Christchurch.⁴⁴ The 2004 data demonstrate that OC concentrations are significantly greater than EC, contrary to that suggested by the 2001/2002 measurements.

The relationship between the measurement methods and the carbon species varies depending on the concentrations detected (see bottom half of Table 8.4). At lower concentrations (25th percentile values), the Series 5400 data were higher than the TOR measurements. However, for the top 50% of the measurements, the Series 5400 produced lower OC and TC, and higher EC, relative to TOR. This was also evident at the 75th percentile level with values of $29.4 \mu\text{g m}^{-3}$ and $14.3 \mu\text{g m}^{-3}$ for TOR OC and OC_5400, $6.3 \mu\text{g m}^{-3}$ and $11.3 \mu\text{g m}^{-3}$ for TOR EC and EC_5400, and $35.4 \mu\text{g m}^{-3}$ and $25.4 \mu\text{g m}^{-3}$ for TOR TC and TC_5400. At maximum concentrations, TOR produced the highest measurements for all carbon species including EC.

Figure 8.2 presents the contribution of TOR EC and TOR OC_{mass} to PM_{2.5}. Although there were only 13 days when PM_{2.5} was measured, during this peak wintertime period, OC_{mass} and EC constituted the majority of mass. On these days, the OC_{mass} contributions ranged from 44% to 87%, EC from 10 to 26% and TC_{mass}⁴⁵ from 65% to 97%. On the highest PM_{2.5} day (20 July 2004), OC_{mass} contributed to 74% of mass and EC to 14%, with a TC contribution of 88%. The Series 5400 was not set at 230°C on that day so a comparison with the Series 5400 contributions to maximum PM_{2.5} could not be made. However, Table 8.5 presents the range of the contributions for the days when the Series 5400 was set at 230°C and 24-hour average data were collected.

The proportions of mass accounted for by OC and EC (Table 8.5) differed depending on the analytical method used, with the TOR method accounting for a greater proportion of mass on average (TOR TC_{mass}, 89%). The maximum 24-hour average PM_{2.5} concentration over these nine days was $76 \mu\text{g m}^{-3}$. On this day, when the TOR data are used, 75% of the mass comprised OC_{mass} and 12% EC (TC = 88% of mass). Conversely, if the Series 5400 measurements are used then OC_{mass} constitutes 37% and EC 23% (TC = 61% of mass).

⁴⁴ The Californian measurements may have been higher if the monitoring had been conducted in winter rather than autumn.

⁴⁵ TC_{mass} represents total carbon mass and is the sum of the OC_{mass} and EC measurements.

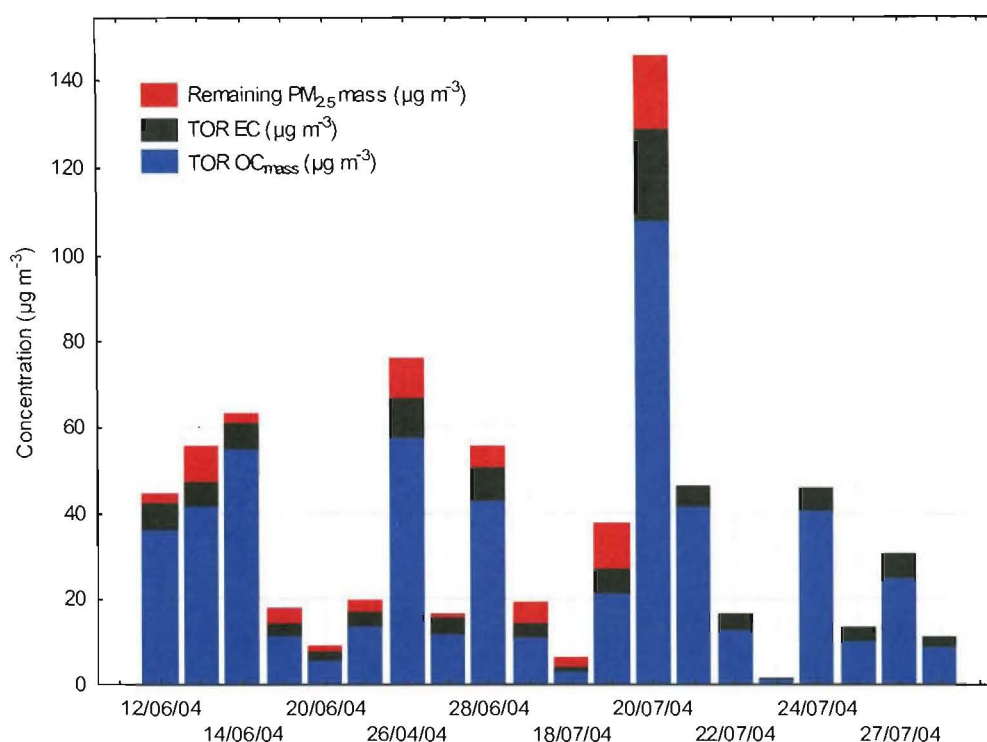


Figure 8.2 TOR carbon contributions to 24-hour average PM_{2.5} (µg m⁻³)⁴⁶.

Table 8.5 Contributions to 24-hour average PM_{2.5} (%) when the Series 5400 was set to 230°C, Christchurch, winter 2004.

	Sample size	Range (%)	Average contributions (%)	Contributions to peak PM _{2.5} (%)
TOR OC _{mass}	9	60-87	73	75
OC _{mass_5400}	9	37-55	44	37
TOR EC	9	10-26	16	12
EC ₅₄₀₀	9	20-23	21	23
TOR TC _{mass}	9	81-97	89	88
TC _{mass_5400}	9	58-77	65	61

8.4.2 Method comparison

Figure 8.3a to c compares the Series 5400 (@ 230°C) data with the corresponding TOR measurements. These include concentrations measured at different times of the day (i.e. 24-hour and 6-hour averages). Differences in the magnitude of the concentrations measured, as indicated by the axes, confirm that the TOR and Series 5400 (@ 230°C) methods do not produce equivalent results. The concentrations measured by the Series 5400 are lower, on average, than those obtained by TOR by approximately 10% for TC and 40% for OC. A clear-cut pattern, where one method consistently over or underestimated the concentrations, was not evident in the EC measurements. This was also reflected in the r^2 values where strong relationships between methods existed for TC ($r^2 = 0.87$) and

⁴⁶ NB: PM_{2.5} were not measured beyond 20/7/2004

OC ($r^2 = 0.88$), and a weaker relationship for EC ($r^2 = 0.64$). It is uncertain why EC was more variable, as it would be expected that OC would always be underestimated and EC overestimated.

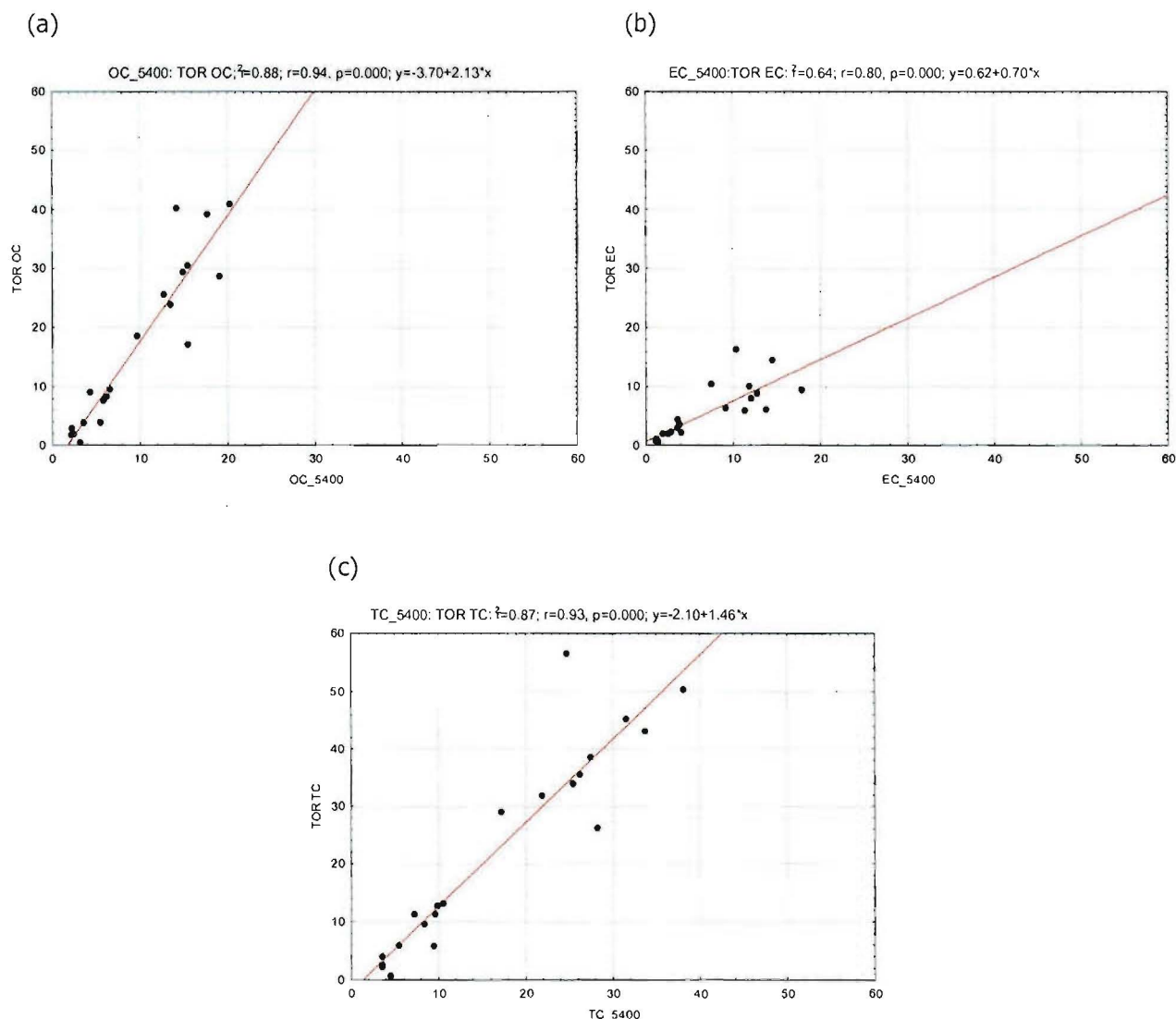


Figure 8.3 Relationship between (a) TOR OC and Series 5400 OC (@ 230 °C), (b) TOR EC and Series 5400 EC (@ 230 °C), and (c) TOR TC and Series 5400 TC (@ 230 °C), 6 hour and 24 hour averages ($\mu\text{g m}^{-3}$), Christchurch, winter 2004.

A Spearman Rank correlation analysis of the 2004 TOR and Series 5400 carbon measurements was conducted to determine the key relationships between species and methods (Table 8.6). The OC measurements provided by both techniques were strongly associated with TC, where coefficients of 1 represented the relationship between the Series 5400 OC and TC, and 0.99 for the TOR OC and TC measurements. All Series 5400 species were closely associated with coefficients of 0.98 for EC and TC, and 0.97 for OC and EC, whereas lower associations were evident for the equivalent TOR data (TOR EC and OC $r^2 = 0.88$, and TOR EC and TC $r^2 = 0.91$). This appeared to impact on the relationship between species and analytical methods, where the TOR OC and TC were strongly

correlated with the Series 5400 measurements (0.92), while EC was slightly weaker (0.86). Good associations were evident between the carbon species and $PM_{2.5}$. The strongest $PM_{2.5}$ relationships were with TOR OC and TOR TC, and the poorest relationship with TOR EC (0.76).

Table 8.6 Relationships between species and analytical methods, Spearman R correlation coefficients (significant at $p < 0.05$), Christchurch, winter 2004.

	TOR OC	TOR EC	TOR TC	OC_5400	EC_5400	TC_5400	$PM_{2.5}$
TOR OC	1.00						
TOR EC	0.88	1.00					
TOR TC	0.99	0.91	1.00				
OC_5400	0.92	0.86	0.93	1.00			
EC_5400	0.89	0.86	0.90	0.97	1.00		
TC_5400	0.91	0.86	0.92	1.00	0.98	1.00	
$PM_{2.5}$	0.85	0.76	0.85	0.83	0.84	0.82	1.00

On the basis of the correlation coefficients and the magnitude of the measurements, it may be concluded that the TOR and Series 5400 (@230°C) techniques produce different results. Nevertheless, it is still useful to determine the significance of this difference using a non-parametric Wilcoxon matched pairs test. This was conducted using Statistica 6.0 and the null hypothesis tested was that the difference between the filter-based and Series 5400 data was zero. The results from the analysis are presented in Table 8.7. Large Z-scores were obtained indicating a low probability that the null hypothesis was true. Consequently, the null hypothesis was rejected for all variables investigated, and the difference between analytical methods deemed significant (p-levels < 0.05). A similar analysis was not conducted on the Series 5400 results at different OC/EC differentiation temperatures, as there were only four and six 24-hour samples available at each setting.

Table 8.7 Summary of results from the Wilcoxon matched pairs test, OC/EC methods comparison, Christchurch, winter 2004.

	Valid	T	Z	p-level
TOR OC & OC_5400	21	24	3.18	0.00
TOR EC & EC_5400	21	44	2.49	0.01
TOR TC & TC_5400	21	37	2.73	0.01

8.4.3 Discussion

The purpose of the OC/EC study was to determine the representativeness of data collected in 2001/2002. The correlation between the OC and EC concentrations, the magnitude of the EC measurements, the proportional abundance of OC and EC, and the impact of these characteristics on the receptor modelling, was of concern. For these reasons, the BC data, rather than EC, were used in

the modelling and supplemented by OC_{mass} . It was accepted that while the OC_{mass} measurements were most likely underestimated, it was best to include as many $PM_{2.5}$ constituents as possible.

Figure 8.4a and b presents the relationships between OC and EC for each of the analytical methods. While positive correlations were evident using both techniques, the relationship between the Series 5400 carbon species (r^2 value of 0.98) was substantially greater than that for TOR (r^2 value of 0.65). Similar coefficients were obtained by a Spearman R correlation analysis, with values of 0.97 for the Series 5400 OC and EC measurements and 0.88 for the TOR data. At face value, the Series 5400 data appear to suggest that the sources of OC and EC do not vary and, consequently, there is little change in the proportional abundance of each species. Conversely, the TOR data are more variable indicating that there are differences in the sources that discharge OC and EC, and/or in the meteorological conditions that lead to secondary OC formation. These variations are particularly useful in the resolution of different factors during receptor modelling. It is uncertain why there is such a strong correlation between the Series 5400 OC and EC measurements. If this technique has the ability to provide equivalent data to TOR, then greater variations in the ratio of OC to EC must be evident at another differentiation temperature (i.e. not 230°C). Although some measurements were conducted at different temperature settings during this study, the sample size was extremely small and further work is required to determine the most appropriate temperature setting for the Christchurch environment.

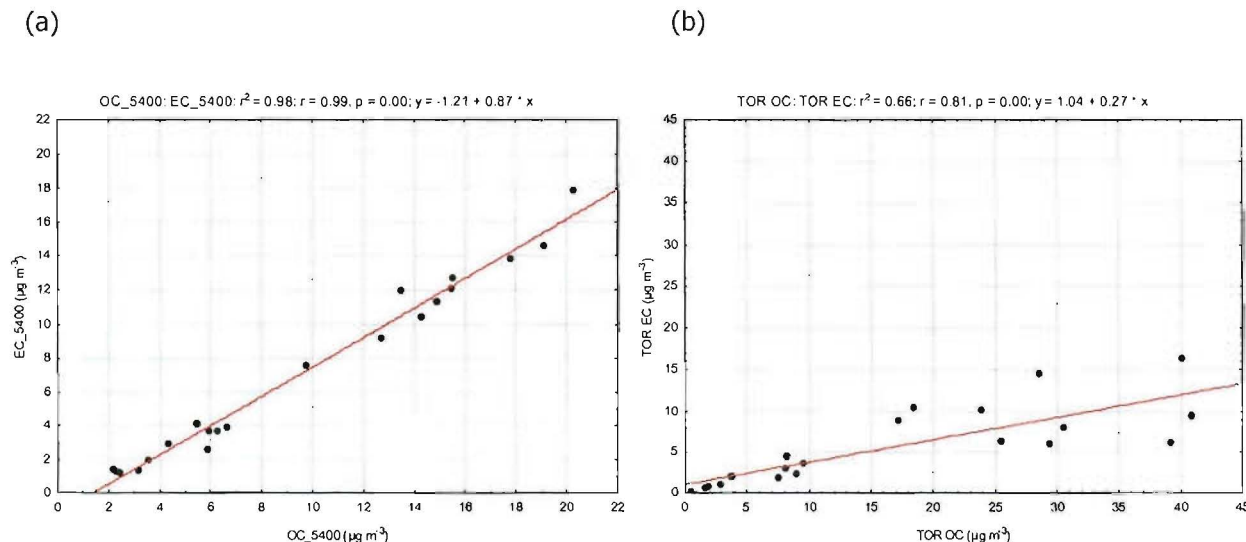


Figure 8.4 Relationship between (a) Series 5400 (@ 230°C) OC and EC measurements, and (b) TOR OC and EC measurements, 6 hour and 24-hour averages ($\mu g m^{-3}$), Christchurch, winter 2004.

The TOR concentrations detected during this study may be evaluated against TOR measurements observed elsewhere. However, the Christchurch concentrations are only representative of a peak wintertime period and are not indicative of annual average values. The 2001/2002 data indicated a

seasonal trend with substantially lower concentrations evident in the summer months (Section 7.3). Comparisons with the data presented in Table 8.2, therefore, are limited to measurements conducted in California during autumn and in Chongju, Korea during winter (Chow *et al.*, 1994; Lee and Kang, 2001). Mean 24-hour average TOR concentrations measured during winter 2004 in Christchurch were $19.8 \mu\text{g m}^{-3}$ for OC and $5.3 \mu\text{g m}^{-3}$ for EC. Maximum 24-hour average TOR concentrations were $79.6 \mu\text{g m}^{-3}$ for OC and $21 \mu\text{g m}^{-3}$ for EC. The means were comparable to the Californian and Korean data, which ranged from 5 to $19.6 \mu\text{g m}^{-3}$ for OC and 4.3 to $7.3 \mu\text{g m}^{-3}$ for EC. Conversely, maximum 24-hour average concentrations were substantially higher in Christchurch compared to maxima, in the range of 9.7 to $33.2 \mu\text{g m}^{-3}$ for OC and 7.8 to $12.1 \mu\text{g m}^{-3}$ for EC, reported by Chow *et al.* (1994) and Lee and Kang (2001). These results confirm that carbon concentrations in Christchurch can be high, regardless of measurement method, and that the magnitude of the previous measurements (2001/2002) is no longer a concern. In addition, the study established that OC and EC are major elemental constituents of wintertime 24-hour average $\text{PM}_{2.5}$ with OC_{mass} constituting 44% to 87% of $\text{PM}_{2.5}$ mass, EC from 10 to 26% and TC_{mass} from 65% to 97%. On the maximum $\text{PM}_{2.5}$ day (20 July 2004), OC_{mass} contributed to 74% of mass and EC to 14%, with a TC contribution of 88%.

The issue of greatest concern was the proportional abundance of OC to EC in the 2001/2002 $\text{PM}_{2.5}$ measurements. This was important as the ratio of OC to EC or TC is often used in source apportionment studies to assist in the interpretation of resolved factors. The 2002 winter measurements indicated mean 24-hour average concentrations of $5 \mu\text{g m}^{-3}$ for OC and $6.6 \mu\text{g m}^{-3}$ for EC, and maximum concentrations of $16.4 \mu\text{g m}^{-3}$ for OC and $27.3 \mu\text{g m}^{-3}$ for EC (Table 8.1). This was contrary to that observed internationally, where OC is generally higher than EC (e.g. Ito *et al.*, 2004; Maykut *et al.*, 2003; Hansen *et al.* 2003). However, the 2004 measurements found that OC was more abundant than EC with 24-hour averages for OC ranging from $0.6 \mu\text{g m}^{-3}$ to $76.9 \mu\text{g m}^{-3}$, and $0.5 \mu\text{g m}^{-3}$ to $21 \mu\text{g m}^{-3}$ for EC. Evidently, the Series 5400 (@ 230°C) did not provide a good representation of OC and EC measurements, relative to the more widely accepted filter-based methods. Therefore, it was highly probable that OC was underestimated and EC overestimated by the Series 5400 in 2001/2002.

Differences in the results provided by the Series 5400 (@ 230°C) and the TOR analytical methods were evaluated further by directly comparing corresponding measurements. Only 21 samples were available, which limited the extent to which a comparison could be made. Nevertheless, it was found that the Series 5400 (@ 230°C) underestimated OC by approximately 40% and TC by 10%, and the EC measurements were variable. These findings were supported by a Wilcoxon matched pairs test that indicated that the difference in results provided by the two analytical methods was significant.

The 2004 study has indicated that the difference between OC measured by TOR and by the Series 5400 (@ 230°C) was substantial. This adversely impacted on the receptor-modelled factors, where OC_{mass} was underestimated relative to BC in the factor loadings matrix. In particular, BC was more

abundant than OC_{mass} in the factor identified as wood combustion, which is unlikely for a wood smoke source, and would not have occurred if reliable OC measures had been used.

Inclusion of OC_{mass} as a separate chemical species is not ideal and can potentially lead to a misinterpretation of the factors resolved. In this regard, it was necessary to revise the analysis presented in Chapter 7. To ensure that most of the mass was accounted for by the chemical species included in the analysis, two options were considered. These included converting the 2001/2002 OC data into TOR OC equivalents using a linear regression equation or using the Series 5400 (@ 230°C) TC data as a single variable, rather than separate OC and EC measurements. However, for the Series 5400 data to be converted into TOR equivalents, the regression equation used must be representative of measurements across an entire year. It was highly unlikely that 21 co-located measurements would allow an accurate conversion equation to be derived. This was demonstrated when the 2001/2002 OC data were converted using the TOR OC and Series 5400 (@ 230°C) linear equation (i.e. $y = -3.70 + 2.13 * x$, where y = TOR OC equivalent and x = OC₅₄₀₀) which resulted in the generation of negative values for most of the summertime measurements. Even if these values were substituted with zero concentrations (i.e. 0 µg m⁻³), this would result in 91% of the summertime OC concentrations comprising zero data. Such a high proportion of zero OC concentrations is unlikely even at that time of year, as sources such as industrial wood boilers, outdoor fires and motor vehicles discharge contaminants including OC during the summer months.

Therefore, the optimal solution was to sum the Series 5400 OC and EC⁴⁷ measurements and use the TC data in the modelling. However, as indicated in Figure 8.3 (c), TC, as measured by the Series 5400, was underestimated relative to TOR by approximately 10%. Despite this, it was less than the underestimate for OC and this limitation would be offset by the benefits of including as much speciated mass as possible in the modelling and by reducing the potential for misinterpretation of the resolved factors.

While it is probable that the temperature setting used during 2001/2002 was the main factor contributing to the differing results between methods, the literature suggests a number of other potential reasons for these discrepancies. Similar intercomparison studies conducted overseas report variations in the results provided by the Series 5400 and filter-based methods (ten Brink *et al.*, 2004; Andrews *et al.*, 2000; Chow *et al.*, 2001). These variations have not only been attributed to differences in temperature settings but also to the particle collection technique, analytical environment, and the CO₂ detector employed by the filter-based (e.g. TOR) and Series 5400 methods. The Series 5400 uses an impactor, with a nominal collection cut-off diameter of 0.14 µm. Consequently, particle bounce, a common issue for impactor systems, could be a potential problem

⁴⁷ It is uncertain how the BC measurements analysed using the M43D digital smoke stain reflectometer compare with TOR measurements. In this regard, EC was preferred, as the total OC and EC measurements had at least been evaluated against the TOR method.

(Turpin *et al.*, 2000; ten Brink *et al.*, 2004). Rupprecht *et al.* (1995), on the other hand, argues that this is not an issue as the impactor is contained within a collector shell. Nevertheless, the cut-off diameter may exclude the smallest particles leading to potentially lower measurements relative to other methods. The Series 5400 measures OC and EC in an oxygen-containing environment, whereas other techniques measure OC in an oxygen-free atmosphere, and EC in a oxygen-containing environment (Lim *et al.*, 2002; Watson and Chow, 2002). As indicated, the temperatures used to differentiate between OC and EC also vary between methods. The setting used to represent OC by the Series 5400 is generally 340°C or lower, whereas filter-based methods such as TOR use temperature settings up to 550°C (Watson and Chow, 2002). Further, the detection methods used to measure the release of CO₂ during analysis are also different. Flame ionisation is used for TOR and non-dispersive infrared for the Series 5400 (Watson and Chow, 2002).

On the basis of these studies, it is uncertain whether a change in the differentiation temperature used by the Series 5400 would provide results equivalent to TOR. Nevertheless, given advantages associated with the instrument including flexibility and costs, it would be worthwhile for additional sampling to be conducted to determine whether a different temperature could provide more comparable data to that generated by TOR.

8.5 Summary

This chapter presented the results of an OC and EC study conducted in Christchurch during the winter of 2004, commissioned in response to concerns regarding the 2001/2002 measurements. Key concerns were the correlation between OC and EC, the magnitude of the EC measurements, the proportional abundance of OC and EC, and the impact of these characteristics on the receptor modelling. The data appeared to be contrary to OC and EC measurements reported in the literature, in particular, the relative abundance of OC to EC. It was suspected that the use of a non-default temperature setting (230°C rather than 340°C) by the Series 5400 to differentiate between OC and EC may have been responsible for these discrepancies.

An intercomparison study was conducted in 2004 to compare measures provided by the Series 5400 (@ 230°C) and the TOR method. Positive correlations between OC and EC were also evident using TOR, but the relationship was not as strong and a higher degree of scatter was evident. The 24-hour concentrations provided by TOR indicated that mean wintertime values were similar to those measured elsewhere, although maximum concentrations were substantially higher in Christchurch than those measured in large cities, such as Los Angeles. The concentrations of OC, as measured by TOR, were considerably greater than EC, contrary to that suggested by the Series 5400 2001/2002 data. On the peak PM_{2.5} day (20 July 2004), OC_{mass} contributed to 74% of mass and EC to 14%, with a TC contribution of 88%.

It was concluded that the two analytical methods used did not provide equivalent results and that the difference was statistically significant. Inclusion of OC_{mass} as a separate variable in the receptor modelling, therefore, was not appropriate and could potentially lead to ambiguous source identification. To allow these measurements to be included, the alternative solution was to use the TC₅₄₀₀ data in the modelling rather than OC and EC. This would prevent the resolution of factors open to misinterpretation, although slightly lower source contribution estimates and reconstructed mass could occur.

Chapter 9: Final source profiles and contributions to PM_{2.5}

9.1 Details of the revised analysis

As indicated in Chapter 8, OC was substantially underestimated by the Series 5400 sampler. Inclusion of this group of compounds as a separate carbon species led to potentially misleading source factors where, for example, EC (as BC) was more abundant than OC_{mass} in the "wood combustion" factor. Generally, wood smoke sources have a greater abundance of OC than EC and if the OC/EC ratios had been used to name this source, it may have been identified as something else. An investigation of OC and EC in 2004, confirmed that the 2001/2002 OC measurements had been under-recorded relative to EC. Consequently, further analysis was required to ensure that the receptor-modelled results were representative. While consideration was given to using BC as the sole carbon species in the modelling, this was not viewed as ideal as it was uncertain how smoke stain reflectometer BC measurements compare with EC analysed by TOR. Rather, the preferred option was to sum the Series 5400 OC_{mass} and EC data to provide measures of TC_{mass} for modelling purposes. While this may slightly underestimate TC relative to other techniques such as TOR, this limitation is offset by the benefits of including as many PM_{2.5} constituents in the analysis as possible.

The receptor modelling discussed in Chapter 7 was repeated in 2004/5 using 15 elemental species instead of 16 (OC_{mass} and BC were deleted and TC₅₄₀₀ data included as TC_{mass}). The parameters used in the modelling were essentially the same as those described in Section 6.5.2. Five factors were selected and multiple results were computed from different starting points, as recommended by Paatero (2000a). The theoretical Q-value for a 15 x 159 concentration matrix was between 1515 and 2385.⁴⁸ The Q-value computed by the modelling was 1420 and the most central solution (f-peak = 0) was used as there was very little rotational freedom evident in the G-Factors. A matrix plot of the G-Factors is included in Appendix 3. The sources identified were the same as those resolved by the modelling presented in Chapter 7, and the contributions of each source to PM_{2.5} were determined using MLR and the G-Factors. The proportion of measured PM_{2.5} accounted for by the modelling is discussed in Chapter 11.

⁴⁸ One definition of the theoretical Q value is: $Q = n \times m - p \times (n + m)$ where p is the number of factors, n is the number of samples and m is the number of species included in the analysis (Phil Hopke, Clarkson University, Potsdam, USA, *pers. comm.*). On this basis, the theoretical Q value would equal 1515. This differs from that indicated in Paatero (2000b), where it is suggested that the theoretical Q value is approximately equal to the number of data points in the concentration matrix. As it is uncertain which rule applies, the theoretical Q is assumed to be between 1515 and 2385.

9.2 Final source profiles

Table 9.1 PMF source profiles, final five-factor solution, Christchurch, 2001/2002.

	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
S	0.00	0.00	0.34	0.16	0.00
Cl	0.07	0.43	0.00	0.00	0.00
Si	0.01	0.00	0.05	0.00	0.06
Fe	0.01	0.00	0.01	0.00	0.02
K	0.15	0.01	0.02	0.00	0.00
Mg	0.00	0.03	0.04	0.02	0.03
Na	0.00	0.32	0.27	0.00	0.08
Ca	0.00	0.01	0.02	0.00	0.01
Zn	0.02	0.00	0.00	0.00	0.00
Cr	0.00	0.00	0.00	0.00	0.01
Ni	0.00	0.00	0.00	0.00	0.00
Al	0.00	0.00	0.01	0.00	0.01
NH ₄ ⁺	0.00	0.00	0.00	0.30	0.00
NO ₃ ⁻	0.07	0.03	0.00	0.35	0.14
TC _{mass}	6.75	0.00	0.00	0.60	1.14
Sum	7.08	0.03	0.76	1.42	1.51
	Wood combustion	Marine aerosol	Aged aerosol	Secondary particulate	Motor vehicles
S			44.1%	11.2%	
Cl	1.0%	51.8%	0.1%	0.2%	0.1%
Si	0.1%	0.2%	7.2%		4.1%
Fe	0.2%	0.1%	1.5%		1.3%
K	2.1%	0.9%	2.3%		
Mg		3.5%	4.8%	1.2%	2.3%
Na		38.6%	34.9%	0.1%	5.1%
Ca	0.1%	1.3%	2.1%		0.5%
Zn	0.2%		0.5%	0.1%	0.1%
Cr			0.4%		0.4%
Ni			0.2%		0.1%
Al			1.7%		0.8%
NH ₄ ⁺			0.1%	20.9%	
NO ₃ ⁻	1.0%	3.2%		24.6%	9.5%
TC _{mass}	95.3%	0.2%	0.1%	41.8%	75.7%

NB: the most significant chemical species present in each factor are highlighted in bold.

The elemental profiles for each source in Table 9.1 are not substantially different to those outlined in Table 7.5 (Chapter 7). The first profile, dominated by carbon and potassium is identified as a wood combustion source. The most abundant species present were TC_{mass} (95%), followed by potassium (2%), chlorine (1%) and nitrate (1%). The proportional abundances were almost identical to the

values in Table 7.5, when OC_{mass} and BC are summed. The second profile was identified as marine aerosol, and again, the chemical constituents were present in similar proportions to that indicated in Table 7.5, with 52% of the mass comprising chlorine, 39% sodium, 4% magnesium, 3% nitrate and 1% calcium. While the first two sources were very similar to those identified previously, there were some variations evident in the profiles of the remaining three sources. This was primarily due to differences in the relative abundance of carbon. For the aged aerosol source, the TC_{mass} contributions decreased from 13% (previous factors) to 0.1% (revised modelling), resulting in an increase in the sulphur (from 39 to 44%) and sodium (31 to 35%) components. For the secondary particulate source, TC_{mass} increased from 31 to 42% of source mass, thereby reducing relative contributions from the other chemical species present. For the motor vehicle source, TC_{mass} decreased (from 80 to 76%), with consequent increases in the proportional abundance of the other chemical species present. These source profiles, and the identification process, are discussed further in Chapter 10.

While these profiles provide a good representation of the main sources contributing to $PM_{2.5}$ in Christchurch, there are several unresolved sources. As discussed briefly in Chapter 7, these include industry, coal burning, soil and diesel vehicles. Box-modelled emission inventory data suggest that contributions from sources such as industry to $PM_{2.5}$ in central Christchurch are minor compared to those from major sources such as residential heating (the primary wood combustion source). Thus, the dominance of particulate from residential heating sources may potentially mask small contributions from other sources to $PM_{2.5}$. However, as these sources are likely to be minor in central Christchurch, the non-resolution of these sources is not of considerable concern.

9.3 Source contribution summary

The G-Factors resolved by the modelling were regressed against $PM_{2.5}$ concentrations using MLR. $PM_{2.5}$ was selected as the dependent variable and the factor scores as the independent variables. The results are shown in Table 9.2.

Table 9.2 Multiple regression coefficients, final five-factor solution, Christchurch, 2001/2002.

	Beta	Std.Err.	B	Std.Err.	t(154)	p-level
Wood combustion	0.81	0.03	13.66	0.47	29.30	0.00
Marine aerosol	0.05	0.02	1.00	0.46	2.18	0.03
Aged aerosol	0.07	0.03	1.62	0.70	2.32	0.02
Secondary particulate	0.09	0.03	1.76	0.68	2.60	0.01
Motor vehicles	0.04	0.03	0.97	0.66	1.48	0.14

All coefficients were significant at $p < 0.05$, with the exception of motor vehicles, where a high degree of error (14%) was evident. Therefore, the motor vehicle estimates were less reliable than those indicated for the other sources. To calculate the daily contributions from each source, each daily

factor score (from the G-Factor matrix) was multiplied by the B coefficient corresponding to that factor. The daily source contributions were then summed to determine daily PMF mass.⁴⁹

Summary statistics for the resolved sources are outlined in Table 9.3. Included in this table are statistics for actual measured $\text{PM}_{2.5}$ and PMF mass. Overall, wood combustion was the most important source of $\text{PM}_{2.5}$ in Christchurch with a median contribution of $6.5 \mu\text{g m}^{-3}$ and a maximum of $89.4 \mu\text{g m}^{-3}$. This was followed by aged aerosol with a median of $1.5 \mu\text{g m}^{-3}$ and a maximum contribution of $4.2 \mu\text{g m}^{-3}$. Secondary particulate and marine aerosol were also notable sources, with medians of 1.3 and $0.7 \mu\text{g m}^{-3}$, and maxima of 6.6 and $5.5 \mu\text{g m}^{-3}$, respectively. Motor vehicles appeared to have the least impact on $\text{PM}_{2.5}$ concentrations with a median of $0.9 \mu\text{g m}^{-3}$ and a maximum contribution of $2.8 \mu\text{g m}^{-3}$.

In summer, the highest contributions (maximum 24-hour concentrations) were from wood combustion ($5.4 \mu\text{g m}^{-3}$), followed by marine aerosol ($4.8 \mu\text{g m}^{-3}$), secondary particulate ($4.4 \mu\text{g m}^{-3}$), aged aerosol ($4.2 \mu\text{g m}^{-3}$), and motor vehicles ($1.6 \mu\text{g m}^{-3}$). While aged aerosol did not make the greatest single contribution to summertime PMF mass, the median concentration of $1.7 \mu\text{g m}^{-3}$ suggests that, overall, this source was a notable contributor. In winter, wood combustion clearly dominated with a median of $16.4 \mu\text{g m}^{-3}$ and a maximum of $89.4 \mu\text{g m}^{-3}$. Secondary particulate was also important, with a median contribution of $2.2 \mu\text{g m}^{-3}$ and a maximum of $6.6 \mu\text{g m}^{-3}$. All sources, apart from aged and marine aerosol, made greater median contributions to $\text{PM}_{2.5}$ during the winter months, and only aged aerosol had higher maximum contributions in summer. Despite this, the aged aerosol contributions did not appear to be seasonally distributed (Figure 10.25 in Chapter 10).

Daily source contributions to PMF mass for all other sources exhibited degrees of seasonality. Wood combustion, secondary particulate and motor vehicles were more substantial during the winter months, whereas the marine aerosol contributions were generally greatest in summer. These variations were linked to seasonal differences in source discharges, and in meteorology. In the wintertime, temperature inversions trap emissions from residential heating and motor vehicles. The contaminants accumulate, react in the atmosphere, and lead to high secondary particulate concentrations. Conversely, residential heaters are rarely used in the summer and strong northeasterly (onshore) winds, typical of summertime meteorology, dilute any emissions present at that time and transport marine aerosol across Christchurch.

⁴⁹ PMF mass is the sum of the daily source contributions in $\mu\text{g m}^{-3}$. These values may be summed, as the daily source contributions were determined from the same filter and have the same sample volume. While strictly these are estimated concentrations, and may be compared directly to $\text{PM}_{2.5}$ measurements, these are generally referred to as "mass". PMF mass and measured $\text{PM}_{2.5}$ are similar but are not always the same. At low concentrations, PMF mass was often greater than $\text{PM}_{2.5}$, and in summer, maximum PMF mass was substantially lower than measured $\text{PM}_{2.5}$. This discrepancy was primarily due to the amount of $\text{PM}_{2.5}$ accounted for by the elemental species measured and is discussed further in Chapter 11.

Table 9.3 Final source contributions to 24-hour average PMF mass ($\mu\text{g m}^{-3}$), summary statistics, Christchurch, 2001/2002.

Total data	Mean	Valid N	Median	Minimum	Maximum	25 th percentile	75th percentile
Wood combustion	13.7	159	6.5	0.001	89.4	1.5	18.6
Marine aerosol	1.0	159	0.7	0.0003	5.5	0.3	1.4
Aged aerosol	1.6	159	1.5	0.0002	4.2	1.1	2.2
Secondary particulate	1.8	159	1.3	0.0005	6.6	0.3	2.9
Motor vehicles	1.0	159	0.9	0.0002	2.8	0.5	1.5
PMF mass	19.0	159	12.4	2.7	97.4	6.1	25.4
PM _{2.5}	19.0	159	11.2	1.1	96.3	5.5	27.1
Summer data	Mean	Valid N	Median	Minimum	Maximum	25 th percentile	75th percentile
Wood combustion	1.5	65	1.2	0.001	5.4	0.5	2.2
Marine aerosol	1.2	65	1.1	0.1	4.8	0.3	1.7
Aged aerosol	1.8	65	1.7	0.5	4.2	1.3	2.3
Secondary particulate	0.7	65	0.4	0.0005	4.4	0.03	0.9
Motor vehicles	0.6	65	0.6	0.0002	1.6	0.3	0.8
PMF mass	5.9	65	5.4	2.7	9.7	4.5	7.3
PM _{2.5}	6.4	65	5.5	1.1	28.3	3.4	7.6
Winter data	Mean	Valid N	Median	Minimum	Maximum	25 th percentile	75th percentile
Wood combustion	22.0	94	16.4	3.0	89.4	8.9	28.8
Marine aerosol	0.8	94	0.6	0.0003	5.5	0.3	1.0
Aged aerosol	1.5	94	1.4	0.0002	3.8	0.9	2.0
Secondary particulate	2.5	94	2.2	0.001	6.6	1.1	3.7
Motor vehicles	1.2	94	1.2	0.001	2.8	0.8	1.7
PMF mass	28.1	94	21.7	6.3	97.4	14.4	36.6
PM _{2.5}	27.7	94	20.9	2.2	96.3	11.9	37.5

A comparison of the source contribution estimates with those derived elsewhere is not presented as it was difficult to find a published study, for a coastal city the size of Christchurch, where PMF was used to apportion sources. Nevertheless, useful source apportionment summaries obtained using PMF are reported in Song *et al.* (2001), Kim *et al.* (2003b), and Kim *et al.* (2003a) for Spokane (population 196,000), Atlanta (population 416,000), Washington DC (population 572,000), Brigantine (population 13,000) and Underhill (population 3,000) in the United States.

Overall, the seasonal trends in the daily source contributions determined by this study appear to correspond with that expected for Christchurch, based on current knowledge of local sources and meteorology. The identification of, and the meteorology associated with, these sources is discussed in greater detail in Chapter 10.

9.4 Average and maximum source contributions

Figure 9.1 and Figure 9.2 present the source contributions to monthly average and monthly maximum PMF mass (24-hour averages) in (a) summer and (b) winter. PMF mass was higher in winter with monthly averages of 20.1 to 30.8 $\mu\text{g m}^{-3}$, and maxima of 52.5 to 97.4 $\mu\text{g m}^{-3}$. In summer, monthly averages of 5.3 to 6.6 $\mu\text{g m}^{-3}$, and maxima of 8 to 9.7 $\mu\text{g m}^{-3}$ were observed. However, summertime maxima were underestimated by the modelling because a disproportionately low amount of $\text{PM}_{2.5}$ was explained by the chemical species measured on those days. Greater uncertainty therefore is associated with these values (refer to Chapter 11 for more details on mass reconstruction).

On a monthly average basis (Figure 9.1), wood combustion dominated wintertime PMF mass (monthly average contributions ranging from 13.7 to 25.7 $\mu\text{g m}^{-3}$), although reasonable contributions were also evident in summer (monthly averages of 0.4 to 2.3 $\mu\text{g m}^{-3}$). Summertime wood combustion sources include the outdoor burning of green waste, not uncommon in rural and semi-rural areas of Christchurch in late summer/early autumn, and wood-fired industrial boilers. Contributions from secondary particulate and motor vehicles were also highest during the winter, with monthly average contributions of 1.6 to 3.6 $\mu\text{g m}^{-3}$ for secondary particulate and 0.7 to 1.6 $\mu\text{g m}^{-3}$ for motor vehicles. In summer, average contributions from these sources were 0.2 to 2.2 $\mu\text{g m}^{-3}$ for secondary particulate and 0.3 to 0.8 $\mu\text{g m}^{-3}$ for motor vehicles. Contributions from aged and marine aerosol, conversely, were greatest during the summer with monthly average contributions of 1.3 to 2.7 $\mu\text{g m}^{-3}$ from aged aerosol and 0.4 to 1.7 $\mu\text{g m}^{-3}$ from marine aerosol. Sea breezes and conditions conducive to photochemical activity (e.g. leading to the formation of Na_2SO_4) are more common at that time. Average monthly wintertime contributions from these sources were 1.1 to 1.9 $\mu\text{g m}^{-3}$ for aged aerosol and 0.5 to 1.1 $\mu\text{g m}^{-3}$ for marine aerosol.

On a monthly maximum basis, other sources were of greater importance in the summer (Figure 9.2). In summer, 0 to 5.1 $\mu\text{g m}^{-3}$ of monthly maximum PMF was attributed to wood combustion, 0 to 4.4 $\mu\text{g m}^{-3}$ to secondary particulate, 1.2 to 3.8 $\mu\text{g m}^{-3}$ to aged aerosol, 0.1 to 2.9 $\mu\text{g m}^{-3}$ to marine aerosol and 0.1 to 1.4 $\mu\text{g m}^{-3}$ to motor vehicles. In the winter, 42.4 to 89.4 $\mu\text{g m}^{-3}$ of monthly maximum PMF mass was attributed to wood combustion, 2.1 to 6.6 $\mu\text{g m}^{-3}$ to secondary particulate, 0.6 to 3.5 $\mu\text{g m}^{-3}$ to aged aerosol, 0.3 to 1.9 $\mu\text{g m}^{-3}$ to motor vehicles and 0.9 to 1.8 $\mu\text{g m}^{-3}$ to marine aerosol.

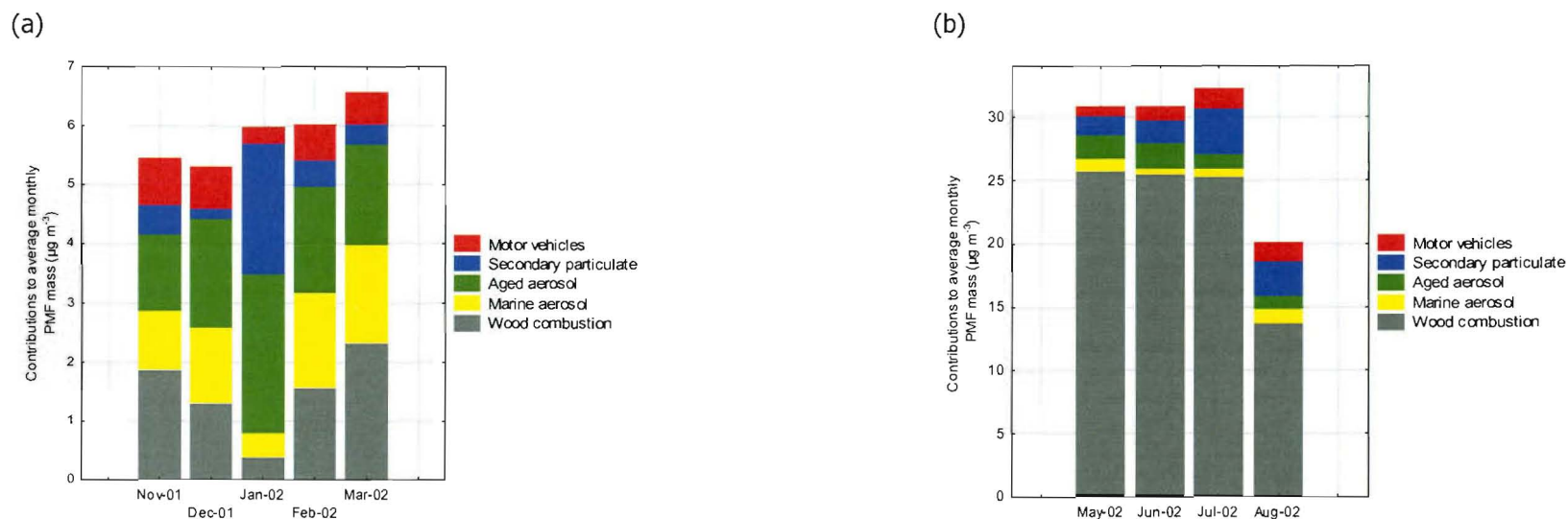


Figure 9.1 Contributions to monthly average PMF mass (24-hour average) in (a) summer and (b) winter, Christchurch, 2001/2002.

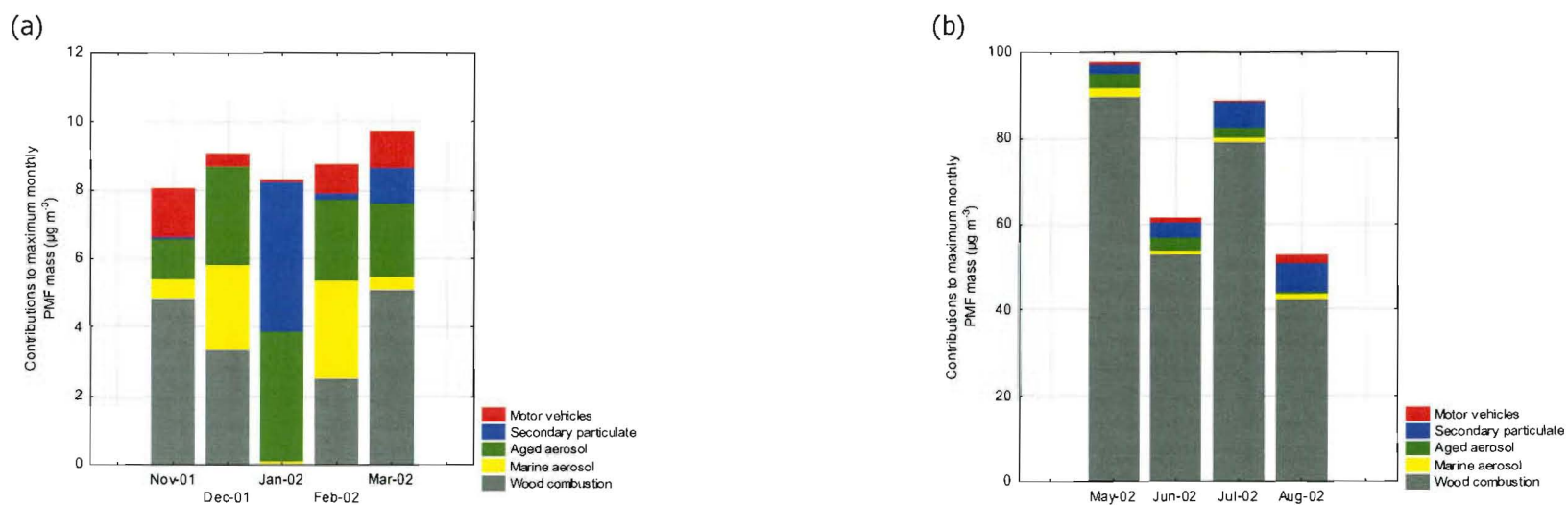


Figure 9.2 Contributions to monthly maximum PMF mass (24-hour average) in (a) summer and (b) winter, Christchurch, 2001/2002.

Figure 9.3 and Figure 9.4 present the source contributions to average and maximum PMF mass in (a) summer and (b) winter. During the summer of 2001/2002, aged aerosol was the most important source on average with a contribution of 31% (Figure 9.3a). This was followed by wood combustion (26%), marine aerosol (21%), secondary particulate (12%) and motor vehicles (10%). However, the ranking of the sources varied when evaluating contributions to the summertime maximum (Figure 9.4a). Wood combustion was the most dominant source (53%) on that day, followed by aged aerosol (22%), motor vehicles (11%), secondary particulate (10%) and marine aerosol (4%). In winter, wood combustion was responsible on average (Figure 9.3b) for 79% of the PMF mass, followed by secondary particulate (9%), aged aerosol (5%), motor vehicles (4%) and marine aerosol (3%). On a maximum basis (Figure 9.4b) the wood combustion contribution increased to 92% of the PMF mass. Contributions from other sources to the wintertime maximum remained low with a 3% contribution from aged aerosol, 2% from marine aerosol, 2% from secondary particulate and 1% from motor vehicles.

While the relative contributions, overall, intuitively make sense, the contributions attributed to the motor vehicle source were lower than expected. It is uncertain why these estimates were so low, but potential causes or contributing factors include the high level of uncertainty associated with the regression coefficients, potential links to the aged aerosol source (note the inverse correlation evident between motor vehicles and aged aerosol in the G-Factors presented in Appendix 3), transformation of motor vehicle emissions into secondary particulate species, or simply because motor vehicle emissions are more localised and less likely to impact on concentrations at Coles Place than other sources.

The sources identified by this study are evaluated in greater detail in the following chapter, and the relative contributions assessed against box-modelled emission inventory data in Chapter 11.

9.5 Summary

Following the completion of the OC and EC study, the speciated dataset was re-analysed. The 2004 study found that OC had been underestimated relative to EC and that it was inappropriate for OC to be included as a separate species in the receptor modelling. The Series 5400 OC_{mass} and EC data were summed to provide a single measure of TC_{mass} for modelling purposes, as it was better to include as many constituents of PM_{2.5} as possible in the analysis.

The five factors resolved by the modelling were identified as wood combustion, marine aerosol, aged aerosol, secondary particulate and motor vehicles. The profiles were not substantially different to those described in Chapter 7. While the resolved factors provided a good representation of the main sources contributing to PM_{2.5} at the St Albans receptor site, industrial, coal-burning, soil, and diesel vehicle sources were not resolved. However, as these are minor sources in the general vicinity of the sample site, their non-resolution is not considered to compromise the analysis.

Daily source contributions were seasonally distributed for most of the sources, with the highest wood combustion, secondary particulate and motor vehicle contributions occurring in winter. The highest marine and aged aerosol contributions occurred in summer, although aged aerosol did not exhibit a distinct seasonal trend. Wood combustion contributed 26% to average summertime PMF mass and 79% of average wintertime PMF mass. However, contributions from this source increased to 53% of summertime and 92% of wintertime mass on a maximum basis. Summertime wood combustion contributions were attributed to outdoor burning or industrial wood combustion sources. Other important summertime sources (on average) were aged (31%) and marine aerosol (21%), and secondary particulate was an important source of wintertime PMF mass (9% on average). Sources such as motor vehicles made minor contributions throughout the year with only 10% of average summertime mass and 4% of average wintertime mass attributed to this source. However, motor vehicles were most likely responsible for the secondary particulate and possibly a proportion of the aged aerosol contributions. Chapters 10 and 11 discuss the modelling results and the sources identified by this study in greater detail.

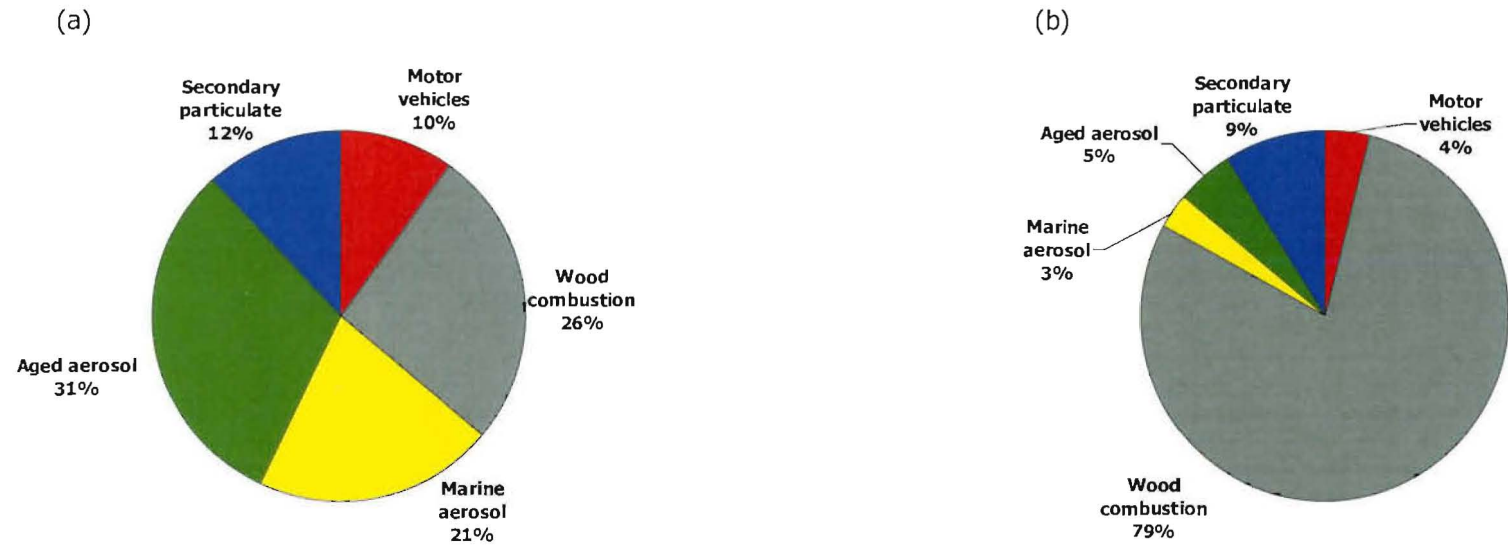


Figure 9.3 Contributions to average PMF mass (24-hour average) in (a) summer and (b) winter, Christchurch, 2001/2002.

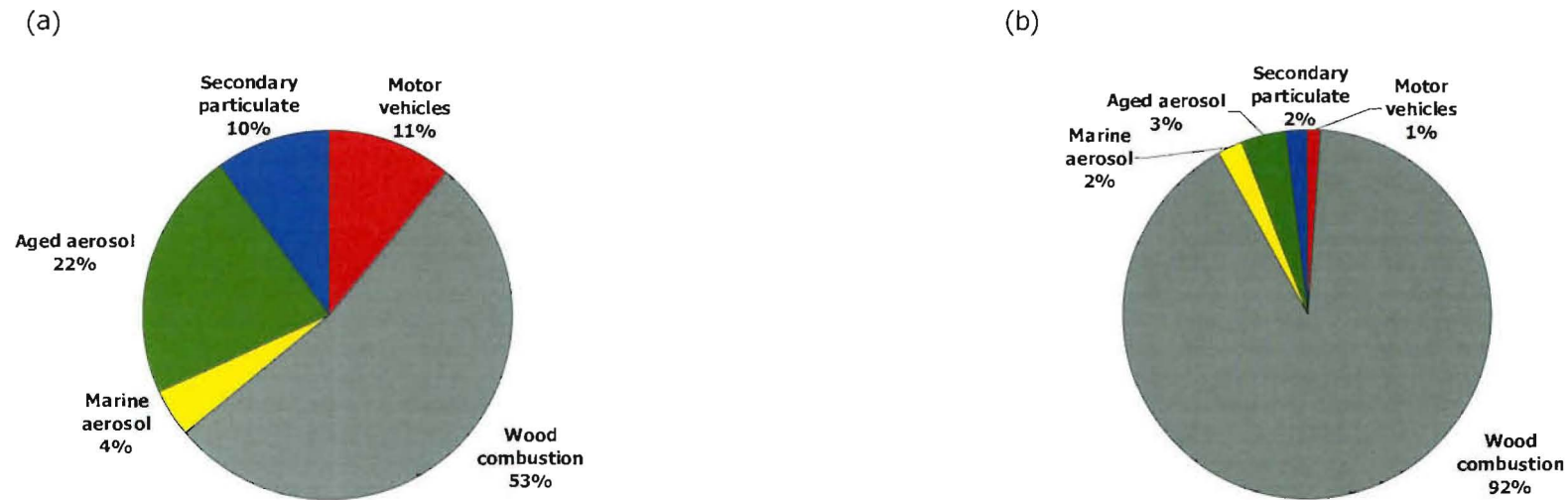


Figure 9.4 Contributions to maximum PMF mass (24-hour average) in (a) summer and (b) winter, Christchurch, 2001/2002.

Chapter 10: Evaluation of the source profiles and their identification

The PMF receptor model groups chemical species into factors (source profiles) and produces factor scores indicating source strength on a daily basis. It does not identify those sources represented by the factors resolved. This is the responsibility of the modeller, and requires good knowledge of the source profiles available in the literature and those determined locally.

The five source profiles resolved by the modelling were identified on the basis of ambient source profile information collected during the study, other New Zealand-based elemental profiles, receptor-modelled profiles described in the literature, and source emission profiles contained in the USEPA's Speciate 3.2 database. However, receptor-modelled profiles are often difficult to use as they are usually presented graphically in the literature (i.e. no original data provided), or expressed as a percentage of mass. Percentages are problematic as these are dependent on the range of species included in the PM mass for each study. Consequently, elemental profiles from other studies are presented qualitatively in this thesis, rather than quantitatively.

The following chapter evaluates the source profiles resolved by this study by reviewing the chemical composition of each source, particle morphology (where possible),⁵⁰ and temporal patterns in various contaminant concentrations and meteorology. This information is used to confirm whether or not the source identification makes sense on a physical basis.

10.1 Wood combustion

10.1.1 Chemical composition

Figure 10.1 presents the elemental profile identified as "wood combustion". Key elemental species were TC_{mass} (95% of mass), potassium (2%), chlorine (1%) and nitrate (1%). The high proportion of carbon present was indicative of a combustion source, as carbon is the main chemical constituent found in combustion-derived PM_{2.5}. However, carbon as a single species cannot be used independently to distinguish between combustion sources such as industry, motor vehicles and wood combustion.⁵¹ Soluble potassium, together with retene and the sugar levoglucosan (not measured during this study), are known wood smoke marker species and are often used to identify wood combustion sources in receptor modelling studies (Chan *et al.*, 1997; Maykut *et al.*, 2003; Polissar *et al.*, 1998; Ramadan *et al.*, 2000; Watson *et al.*, 1991; Fine *et al.*, 2002; Schauer *et al.*, 2001).

⁵⁰ Several filters representing peak source days were analysed using SEM by Perry Davy of Greater Wellington Regional Council. These have been included for illustrative purposes, where available.

⁵¹ Different carbon fractions, if included separately, may be used to differentiate between motor vehicle and residential heating sources.

Potassium was most prominent in this factor (relative to the other factors) and although the soluble fraction was not explicitly measured, it was assumed that any potassium linked to carbon was present in a soluble form.

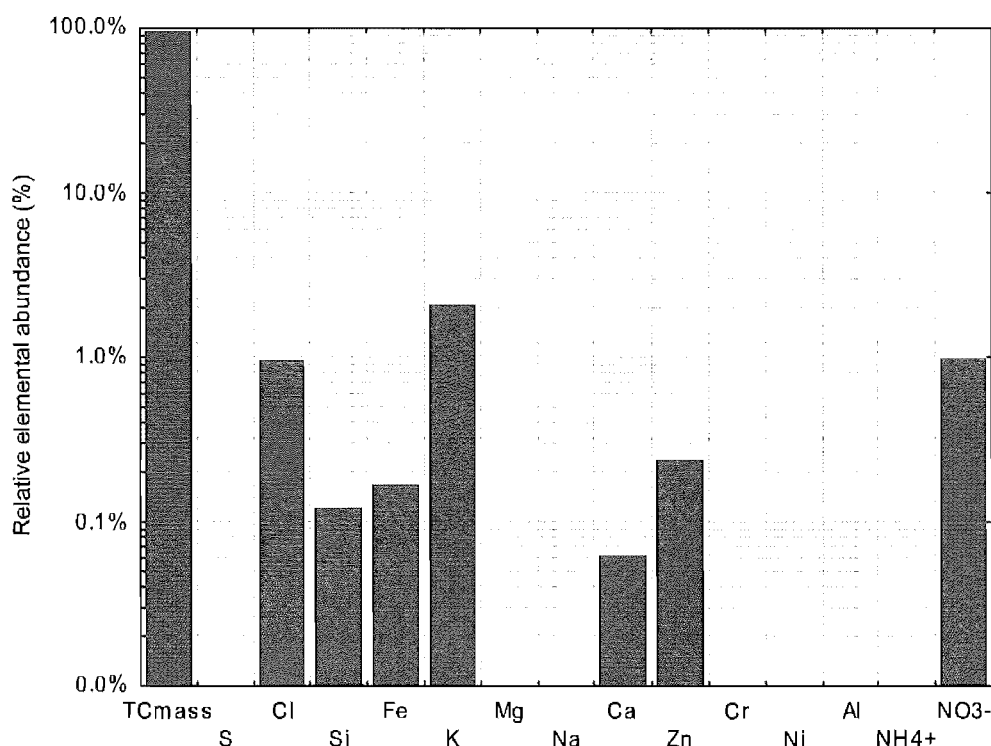


Figure 10.1 Wood combustion profile, relative elemental abundance, Christchurch, 2001/2002.

Table 10.1 presents the source profiles used to identify this factor, including ambient source profiles measured during the study, direct source emission profiles, and those resolved by receptor modelling studies. The most reliable profiles are those collected by direct source emission tests, as these are not likely to include emissions discharged from other sources. However, these do not necessarily represent the wide range of wood combustion sources available, or account for the chemical and physical changes that occur in $PM_{2.5}$ prior to being measured at a receptor site. The ambient source profiles were compiled to take these changes into account, but possibly include minor contributions from other sources.

The main chemical constituents found in wood smoke emissions, and in the profiles of wood combustion factors (Table 10.1), were carbon (organic and elemental), potassium and sulphur. These species, with the exception of sulphur, were included in the factor profile identified as "wood combustion" by this study. It is uncertain why sulphur was not present but it may not be as an important constituent of wood smoke in Christchurch as that indicated elsewhere, or it may have reacted in the atmosphere to form secondary particulate and become associated with another factor (e.g. sulphur to sulphate and thus grouped into the secondary particulate factor). Other New Zealand

source and receptor-modelled profiles have included sulphur but found that it was less abundant than other elemental species. Markwitz *et al.* (2003) found EC, sodium, sulphur, chlorine and potassium in emissions sampled during a New Zealand real-life wood burner emissions study (OC was not measured), although the relative abundances of chlorine, potassium and sodium were greater than that for sulphur. Wilton (2003) also observed greater elemental abundances for EC, silicon, calcium and zinc, relative to sulphur (NB: only 1% was attributed to potassium in that study). These findings were supported by Paterson (2002), who resolved a wood combustion profile during a preliminary source apportionment assessment in Christchurch - where carbon, chlorine and potassium contributions were more substantial than sulphur.

Table 10.1 Elemental profiles for wood combustion sources (reference sources listed).

	C	Na	Mg	Al	Si	S	Cl	K	Ca	Cr	Fe	Ni	Zn	NH ₄ ⁺	NO ₃ ⁻
Ambient source profiles (residential backyards)	NM	✓	✓	✓	✓	✓	✓	✓	✓		✓		✓	NM	NM
Other New Zealand profiles															
Wilton (2003)	NM	✓		✓	✓	✓		✓	✓		✓		✓		
Paterson (2002)	✓					✓	✓	✓							
Scott (2004)	✓	✓			✓	✓	✓	✓	✓		✓		✓	NM	NM
Markwitz <i>et al.</i> (2003)	✓	✓					✓	✓						NM	NM
International profiles															
Maykut <i>et al.</i> (2003)	✓							✓					✓		
Lewis <i>et al.</i> (2003)	✓							✓							
Polissar <i>et al.</i> (1998)	NM	✓	✓	✓		✓		✓	✓		✓		✓		
Ramadan <i>et al.</i> (2000)	✓	✓						✓							
Polissar <i>et al.</i> (2001)	NM		✓		✓	✓		✓			✓				
Kim <i>et al.</i> (2003b)	✓			✓	✓			✓							
Song <i>et al.</i> (2001)	✓					✓		✓	✓				✓		
OMNI ES (1989)	✓					✓	✓	✓							✓
Speciate 3.2 database (USEPA)	✓					✓	✓	✓							
Residential wood stove composite Speciate 3.2 database (USEPA)	✓	✓			✓	✓	✓	✓					✓	✓	✓
Wood-fired boiler, Speciate 3.2 database (USEPA)	✓	✓				✓	✓	✓	✓		✓				
Fine <i>et al.</i> (2002)	✓				✓	✓	✓	✓					✓	✓	✓
Chow <i>et al.</i> (2004)	✓	✓			✓	✓	✓	✓	✓					✓	✓
PMF wood combustion	95%				0.1%		1%	2%	0.1%		0.2%		0.2%		1%

NM: Not measured

On the strength of the association between carbon and potassium, this source was identified as wood combustion. The relative abundance of potassium was greatest in this factor, relative to the other source profiles. As potassium may be found in a variety of wood combusted emissions including biomass burning, residential heating, outdoor burning and wood-fired boilers, the source was identified broadly as "wood combustion" rather than a "residential heating" source.

10.1.2 Contributions to mass

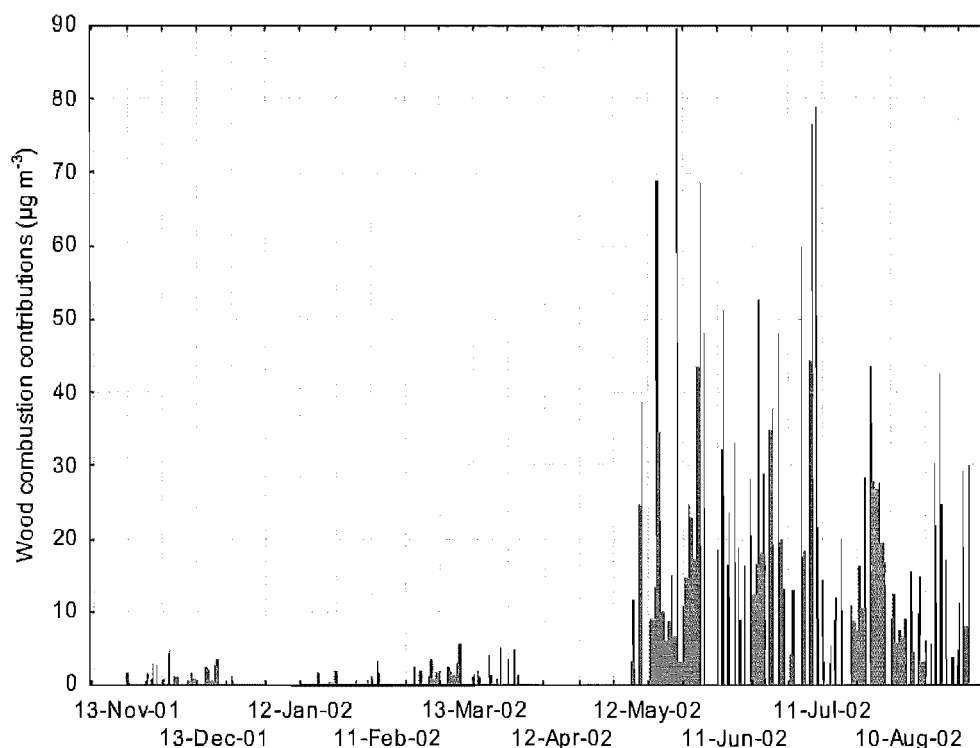


Figure 10.2 Daily wood combustion contributions to PMF mass (24-hour averages), Christchurch, 2001/2002.

Figure 10.2 presents daily wood combustion contributions to PMF mass. A seasonal pattern is evident with lower contributions in the summer and higher contributions in winter. As indicated in Table 9.3, median wood combustion contributions were $1.2 \mu\text{g m}^{-3}$ in the summer and $16.4 \mu\text{g m}^{-3}$ in the winter. Maximum contributions were $5.4 \mu\text{g m}^{-3}$ in the summer and $89.4 \mu\text{g m}^{-3}$ in the winter. This corresponds with emission patterns in Christchurch, where wood combustion activities are limited in summer (outdoor burning, wood-fired boilers), and substantially greater in winter when wood is widely used as a residential heating fuel. It has been estimated that on an average winter's day, approximately 24,000 wood burning appliances (including pellet burners) are used for residential heating in central Christchurch, and 54,000 across the built-up areas of the city (Scott and Gunatilaka, 2004).

The seasonal trend in wood smoke contributions is also supported by the findings of a study conducted by Krivácsy *et al.* (2005) which attributed differences in the chemical composition of PM in summer and winter, to source origin. Carbohydrate derivatives, associated with the combustion of biomass material, were of greater importance during the winter and absolute concentrations of these derivatives were greater in Christchurch than in larger cities like Auckland. Dehydroabietic acid, which was present in Christchurch at concentrations four times higher than Auckland, was thought to be derived from the combustion of coniferous wood. This compound was also detected during the

summer months but at an order of magnitude lower. Key wood smoke tracer species such as levoglucosan were also found.

10.1.3 Characteristics of the peak wood combustion event

Review of the peak wood combustion event during the course of the study - and the source contributions, elemental composition, particle characteristics, diurnal contaminant concentrations and meteorological conditions associated with it - assists in evaluating whether the physical characteristics of this particular factor make sense. Wood combustion contributions are most likely to be greatest under temperature inversion conditions, when wind speeds are low, temperatures are cool and skies are clear.

The five peak wood combustion events, which occurred in May and July 2002, are listed in Table 10.2. Twenty-four hour average concentrations of SO₂, NO, NO₂, NO_x, CO, PM_{2.5}, PM₁₀ (measured by a high volume sampler)⁵² and PMF mass is included, together with the wood combustion contributions.

Table 10.2 Five peak wood combustion events, 24-hour average data, Christchurch, 2001/2002.⁵³

Date	SO ₂ ($\mu\text{g m}^{-3}$)	NO ($\mu\text{g m}^{-3}$)	NO ₂ ($\mu\text{g m}^{-3}$)	NO _x (ppb)	CO mg m ⁻³	PM _{2.5} ($\mu\text{g m}^{-3}$)	PM ₁₀ Hivol ($\mu\text{g m}^{-3}$)	Wood combustion ($\mu\text{g m}^{-3}$)	PMF mass ($\mu\text{g m}^{-3}$)
22/5/02	20	-	-	-	6	96	111	89	97
9/7/02	13	85	29	78	3	95	96	79	89
8/7/02	13	116	37	105	3	69	89	77	87
15/5/02	6	-	-	-	4	84	92	69	78
30/5/02	17	-	-	-	3	65	53	69	76

Estimated source contributions and key elemental constituents

The peak wood combustion event occurred on 22 May 2002. Figure 10.3a and b presents the estimated source contributions, and the main elemental species present in PM_{2.5}, for that day.

The PM_{2.5} concentration on 22 May 2002 was 96 $\mu\text{g m}^{-3}$ and PMF mass was slightly overestimated at 97 $\mu\text{g m}^{-3}$. Approximately 92% of the PMF mass was of wood combustion origin, with the remainder comprising aged aerosol (3%), secondary particulate (2%), marine aerosol (2%) and motor vehicles

⁵² Refer to the Environment Canterbury website for descriptions of the monitoring methods used: www.ecan.govt.nz.

⁵³ The data presented in Table 10.2 show that on one of the five days indicated, PM_{2.5} concentrations exceeded the PM₁₀ measurements (30 May 2002). Normally this should not occur as PM_{2.5} is a subset of PM₁₀. It is uncertain why this happened in this instance, but as there was no obvious basis for invalidating the data (e.g. incorrect flows, etc), the concentrations were retained in the dataset. Also of note, is the overestimation of mass by PMF on three of the five days. This also led to higher wood combustion estimates than PM_{2.5} on some days and may be related to a combination of factors, including the adequacy of the conversion factor used to estimate TC_{mass}, and the MLR coefficients used to scale the data up to PM_{2.5} equivalents. However, as a whole, PM_{2.5} was modelled effectively and some over and underestimation of individual data points is expected.

(1%). The main elemental species were TC_{mass} (89%), followed by sulphur (2%), chlorine (2%), sodium (2%), nitrate (2%), potassium (1%), and ammonium (1%).

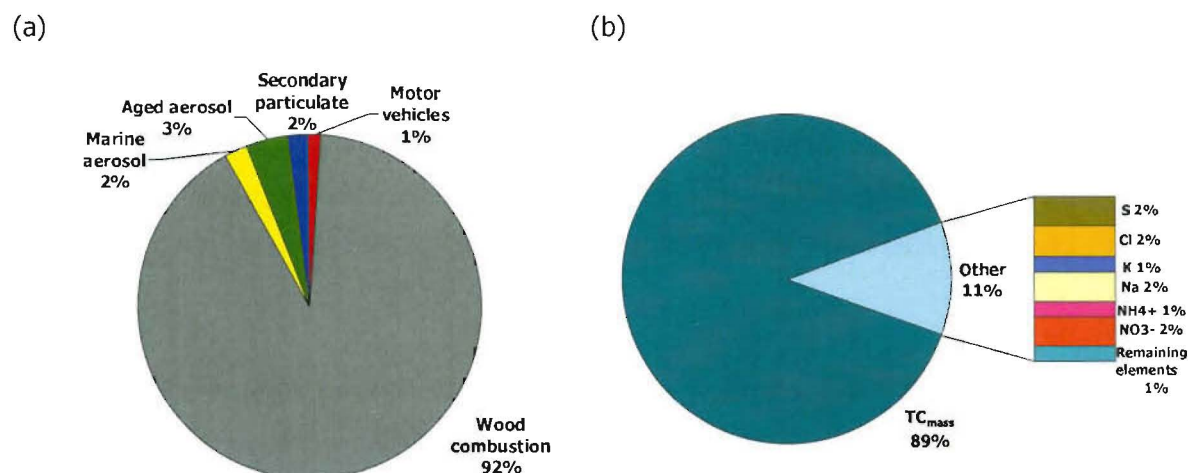


Figure 10.3 Contributions to (a) PMF mass and (b) to the sum of the PM_{2.5} constituents on 22 May 2002, Christchurch.

Particle characteristics

Figure 10.4a to d presents a selection of SEM micrographs of particles found on the filter of 22 May 2002. High particulate loadings are evident in Figure 10.4a and b where “sticky” agglomerations of amorphous particles cover the filter surface (NB: these are magnified by x5,500 and may be compared with photographs of similar resolutions in the other sections). An elemental mapping program was used to evaluate the chemical composition of particles on the filter and carbon was identified as the primary elemental constituent present. The denseness and “sticky” appearance of the particulate mass suggested that the carbon compounds were organic in composition and possibly “aged” in nature (Cachier, 1998).

Multiple types of particles are evident (small crystals and spheres). Individual particles - depending on their chemical composition and the impact of combustion temperatures and atmospheric conditions - take on different forms. Mavrocordatos *et al.* (2002) suggest that both soluble organic and inorganic salts may be present in emissions from wood combustion. Figure 10.4c and d show two crystal structures that were found on the filter. The crystals were rod-like or cylindrical in form and an elemental scan of the particles illustrated in Figure 10.4c indicated a carbon, oxygen, sodium, silicon, chlorine and potassium composition. The particle in Figure 10.4d was of a similar composition but also included sulphur. While these may constitute potassium salts of some sort, the form potassium takes when discharged in wood smoke is not certain. Inorganic salts such as potassium chloride (KCl) are present as solids at very low relative humidity and become a saturated aqueous solution with increasing humidity. This process is referred to as deliquescence and when relative humidity decreases, the water evaporates, and the particle re-crystallises (Pilinis and Pandis, 1995).

It is not known whether the particles were deposited on the filter in this form, or were transformed during sample storage or transit.

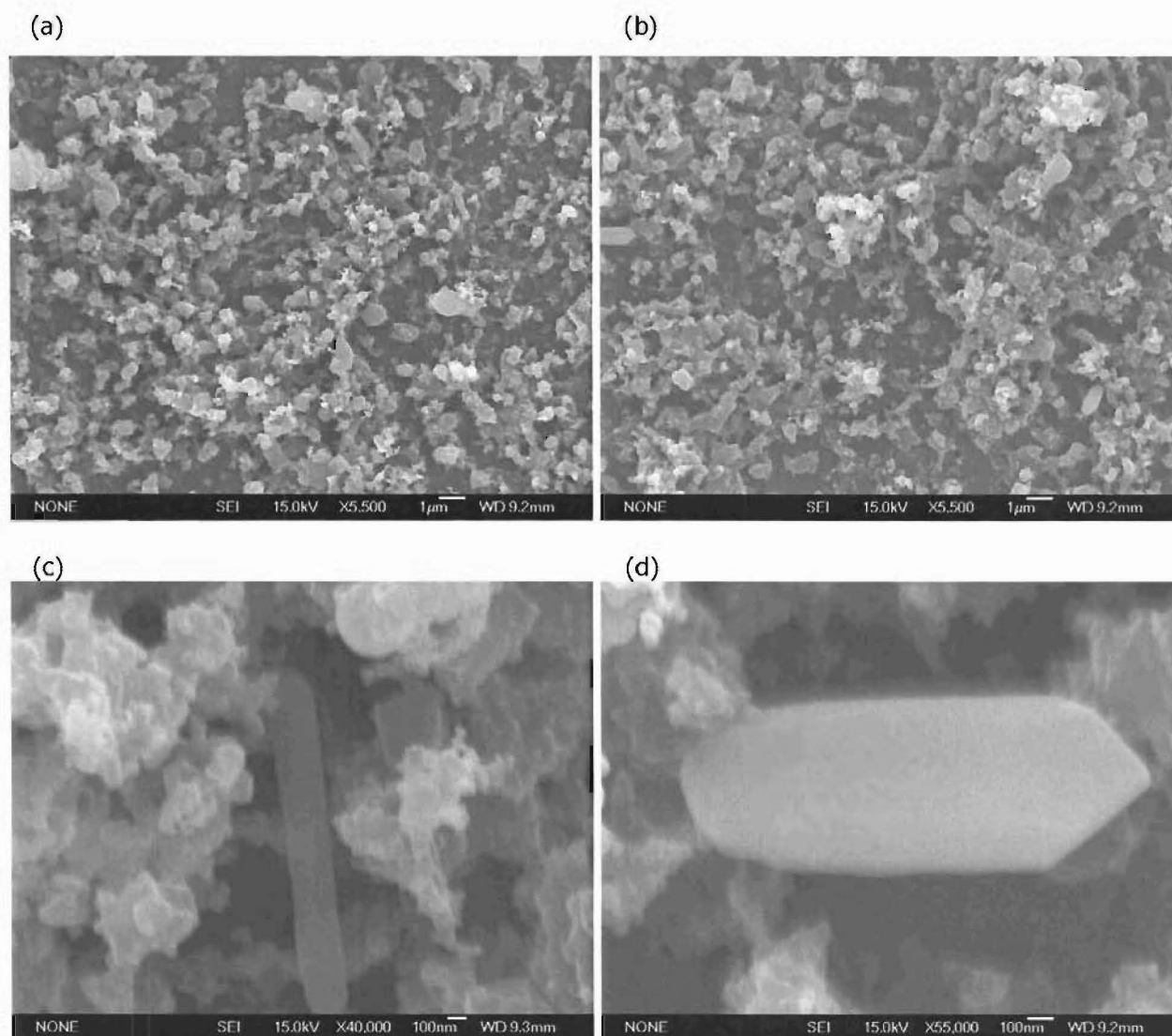


Figure 10.4 Particles sampled onto a polycarbonate filter on 22 May 2002, Christchurch.

There are few SEM micrographs of wood smoke emissions available for direct comparison in the literature and those that are available are often at different resolutions. Nevertheless, Figure 10.5a and b has been included to illustrate differences in the particles sampled from wood smoke. The particles presented in Figure 10.5a were published by Colbeck *et al.* (1997) and were collected from smouldering wood shavings. Conversely, those published by Murr and Bang (2003) were sampled outdoors in a wood burning area (Figure 10.5b). These indicate that particle shape can vary depending on the wood combustion source and fuel being burnt. Some caution is advised when attempting to differentiate between particles using morphological characteristics alone, as those presented in Figure 10.5b are not dissimilar to diesel particles (Figure 10.12c).

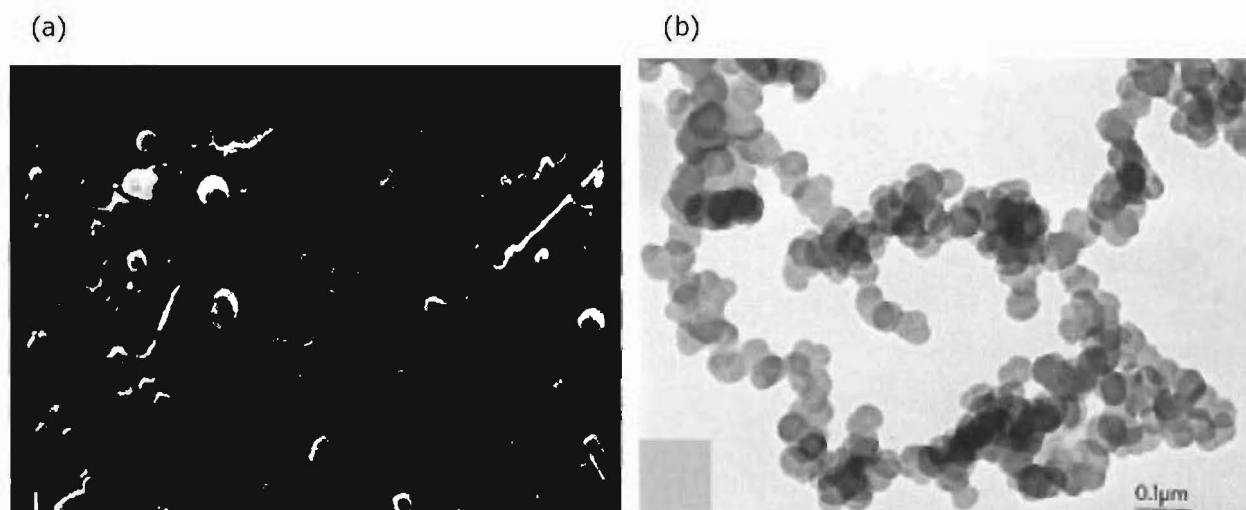


Figure 10.5 Particles from (a) the combustion of wood shavings and (b) in an outdoor wood combustion aggregate.

Despite the difficulties associated with identifying source origin on a morphological basis, the SEM micrographs demonstrate that a variety of particles were present on 22 May 2002, including “sticky” organic agglomerations and inorganic potassium salts. This finding is consistent with what would be expected of a wood smoke source in Christchurch.

Temporal variations in meteorology and contaminant concentrations

Figure 10.6a to d presents hourly average contaminant concentrations (including PM_{10} measured by TEOM, SO_2 and CO), temperature difference,⁵⁴ wind speed and direction, ambient temperature, and relative humidity measured at Coles Place, St Albans, on 22 May 2002.

At 10 am,⁵⁵ a morning PM_{10} peak coincided with a mild temperature inversion. Wind speeds were from a northwest to northeasterly direction and were present at low speeds throughout the day. Winds were calm overnight and increased in speed during the early hours of the morning. Daytime temperatures were warm during this event (up to 20°C) with cooler overnight temperatures and a minimum of 6°C. A strong temperature inversion was evident from 5 pm and remained in place until the following morning. PM_{10} , CO and SO_2 concentrations increased as the inversion was established, and PM_{10} and CO peaked around 10.30 pm, decreasing to low levels by 4.30 am. SO_2 followed a similar pattern, but peaked slightly later in the morning and earlier in the evening. The differences in

⁵⁴ Temperature is measured at Coles Place at a height of 1 m (T_1) and 6 m (T_2). Under inversion conditions, temperature increases rather than decreases with height and a negative “temperature difference” (i.e. $T_1 - T_2 = -x$) indicates the presence of an inversion.

⁵⁵ The continuous measurements indicated on the hour represent the average measurement for the hour previous. Therefore, continuous data from 10 am to 9 am are directly comparable to the 9 am to 9 am sampling period adopted by this study.

the timing of the contaminant concentrations may be due to variations in emission sources or the influence of atmospheric chemical processes.

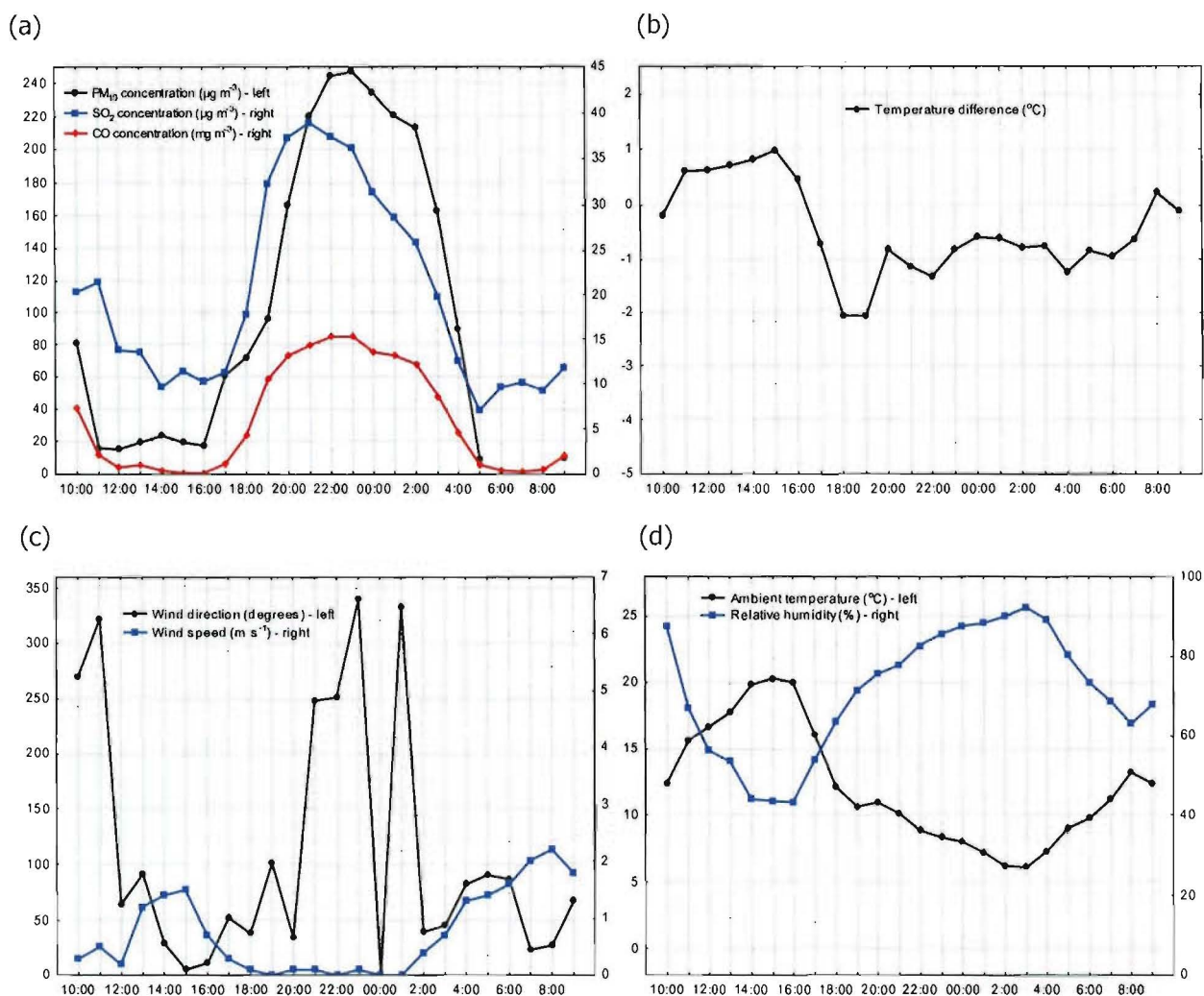


Figure 10.6 Hourly average contaminant and meteorological data on 22 May 2002, St Albans, Christchurch.

Appendix 3 presents a matrix plot of sources and various meteorological variables including wind speed, temperature and relative humidity. The scatter plots for wood combustion suggest that contributions from this source are highest at low wind speeds, low temperatures and moderate humidity. The correlation analysis presented in Appendix 4 indicates that the strongest associations with the other sources and meteorological variables occur in the winter months. For wood combustion, there is a weak positive correlation with aged aerosol (0.54), secondary particulate (0.41) and a strong negative correlation with wind speed (-0.72). A positive correlation with other contaminant sources is expected as the same conditions that lead to high wood combustion aerosol (e.g. low winds and temperature inversions) are also likely to lead to high contributions from other sources.

For the remaining four events indicated in Table 10.2, diurnal profiles of the key meteorological variables, wind speed and temperature difference, and PM₁₀ concentrations are included at Appendix 5. The diurnal pattern in hourly average PM₁₀ is similar for each of these events, where concentrations initially peaked in the morning (30 to 80 µg m⁻³), followed by a period of relatively low concentrations. By 4 pm, concentrations started to increase and peaked at concentrations of 230 to 280 µg m⁻³ between the hours of 10 pm and 1 am. The concentrations then gradually decreased down to low levels by 6 am. On occasion, however, concentrations declined at a quicker rate in response to increased wind speeds. The meteorological variables also indicate that temperature inversions were typical of wood combustion events, as were low wind speeds. While most events were also characterised by low temperatures, as indicated in Figure 10.6d, wood combustion contributions may also occur on relatively warm days provided that the key characteristics – strong inversions and low wind speeds – are evident overnight.

10.2 Motor vehicles

10.2.1 Chemical composition

Figure 10.7 presents the elemental profile identified as “motor vehicles”. Key elemental species were TC_{mass} (76% of mass), nitrate (10%), sodium (5%), silicon (4%), magnesium (2%) and iron (1%). The high proportion of carbon present was indicative of a combustion source, and combined with the presence of soil-related species (silicon and magnesium) and metals (nickel, aluminium and zinc), suggests a motor vehicle origin. These species are commonly found in emissions from engine combustion, the re-entrainment of road dust, and are discharged during the wear-and-tear of brake pads.

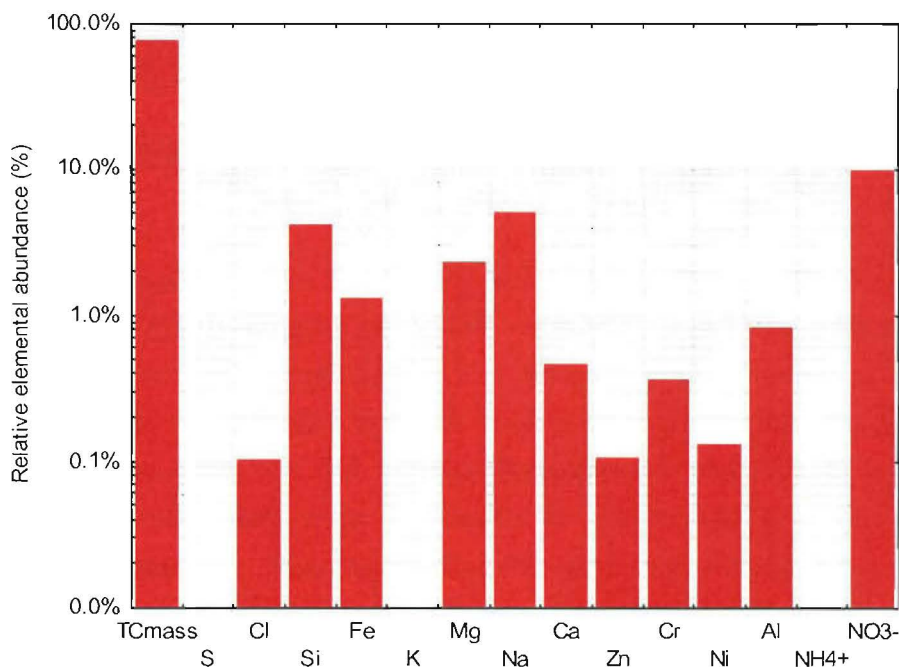


Figure 10.7 Motor vehicle profile, relative elemental abundance, Christchurch, 2001/2002.

Table 10.3 presents the source profiles used to identify this factor, including ambient source profiles measured during the study, direct source emission profiles, and those resolved by receptor modelling studies. Both diesel and petrol-fuelled vehicle profiles are included, and emissions vary by motor vehicle and fuel type. Although the direct source emission profiles are the most reliable, these do not necessarily represent the range of vehicles available in New Zealand or account for chemical transformation in emission products between source and receptor. The ambient source profiles were compiled to take these changes into account, but are likely to include minor emissions from other sources.

Table 10.3 Elemental profiles for motor vehicle sources (reference sources listed).

	C	Na	Mg	Al	Si	S	Cl	K	Ca	Cr	Fe	Ni	Zn	NH ₄ ⁺	NO ₃ ⁻
Ambient source profiles, Colombo St and Riccarton Rd		✓	✓	✓	✓	✓	✓	✓	✓	✓	✓		✓	NM	NM
Other New Zealand profiles															
Davy <i>et al.</i> (2002b)	EC		✓	✓	✓	✓			✓	✓		✓	✓		
Trompetter <i>et al.</i> (2005) – petrol	EC	✓	✓	✓	✓	✓	✓		✓						
Trompetter <i>et al.</i> (2005) – diesel	EC	✓	✓	✓	✓	✓									
Paterson, 2002	✓														
International profiles															
Lewis <i>et al.</i> (2003) – petrol	✓														
Lewis <i>et al.</i> (2003) – diesel	✓										✓				
Maykut <i>et al.</i> (2003) – petrol	EC			✓				✓	✓				✓		
Maykut <i>et al.</i> (2003) – diesel	✓				✓					✓	✓	✓	✓		
Kim and Hopke (2003) – petrol	✓							✓							
Kim and Hopke (2003) – diesel	✓		✓		✓				✓		✓		✓		
Kim <i>et al.</i> (2003a)	✓				✓						✓			✓	
Polissar <i>et al.</i> (2001)	EC	✓	✓	✓	✓	✓		✓	✓		✓		✓		
Ramadan <i>et al.</i> (2000) – petrol	✓														
Ramadan <i>et al.</i> (2000) – diesel	EC										✓				
Polissar <i>et al.</i> (1998) – petrol	EC			✓	✓	✓		✓	✓		✓		✓		
Song <i>et al.</i> (2001)	✓				✓			✓	✓		✓		✓		
OMNI ES (1989) – heavy duty diesel	✓	✓			✓	✓	✓	✓	✓		✓		✓	✓	✓
Speciate database (USEPA) – heavy duty diesel	✓			✓	✓	✓	✓		✓		✓	✓	✓		
Speciate database (USEPA) – light duty diesel	✓				✓	✓	✓		✓				✓		
Chow <i>et al.</i> (2004) – motor vehicle composite	✓	✓			✓	✓	✓	✓	✓		✓		✓		✓
PMF motor vehicle	75.5%	5.1%	2.3%	0.8%	4.1%	0.1%	0.1%	0.5%	0.4%	1%	0.1%	0.1%	0.1%		10%

NM = not measured

The profiles in Table 10.3 demonstrate the variation inherent in the elemental composition of motor vehicle emissions. Fuel composition, the nature of the motor vehicle fleet, and air pollution control requirements in the different countries are responsible for the variations. Nevertheless, the main

chemical constituents found in motor vehicle emissions, and in the profiles of motor vehicle factors, were carbon (OC and EC), silicon, calcium, iron and zinc. Other species commonly associated with motor vehicles, but not included in the receptor modelling due to the amount of zero and below detection limit data, were copper, manganese, vanadium, titanium, bromine and lead. The factor identified by this study as "motor vehicles" contained the key species indicated above, as well as nitrate, sodium, magnesium, chlorine, chromium, nickel and aluminium. Soil-related species and metals associated with mechanical degradation are often found in motor vehicle profiles, but few report the presence of sodium and magnesium. These species are normally associated with marine aerosol and it may be that uncertainties associated with these elements were not sufficiently allocated. However, it is interesting to note that both species were included in other New Zealand motor vehicle profiles (e.g. Trompetter *et al.*, 2005).

Only a single factor that could be attributed to motor vehicles was resolved. The presence of heavy metals such as chromium and nickel implied that diesel emissions may be included in this factor (although sulphur was not found). This factor was also most likely, out of all the factors, to represent petrol-fuelled vehicle sources. In this regard, it was considered to constitute a mixed vehicle source. If OC and EC had been measured accurately, and were included as separate components in the analysis, it may have been possible to determine whether petrol vehicles did or did not comprise part of the factor. A greater EC to OC ratio would suggest that the factor was dominated by diesel vehicles rather than petrol, whereas, a relative increase in OC would be indicative of petrol-fuelled vehicles.

As part of the PMF modelling process, the daily G-Factors (source strengths) for each source were plotted against each other to determine the degree of rotational freedom evident, and whether the best solution had been derived. These are attached at Appendix 3. While, in general, there was a degree of independence between the different factors, there was a pronounced negative correlation between the motor vehicle and aged aerosol factors. When motor vehicle contributions were high, aged aerosol was low, and vice versa. It is uncertain why this was the case but it suggests a link. Possible explanations are that aged aerosol constitutes a secondary component of motor vehicle emissions (i.e. motor vehicle emissions have reacted photochemically to produce aged aerosol), or that the meteorological or emission conditions that lead to aged aerosol are always different than that of motor vehicles. If the latter were true, however, a pattern of contributions such as that indicated for wood combustion and marine aerosol would occur, where one or the other source is dominant. A photochemical link is more likely as this type of distribution could be expected where primary motor vehicle emissions are only partially transformed into aged aerosol on some days, and a more complete transition occurs on other days.

10.2.2 Contributions to mass

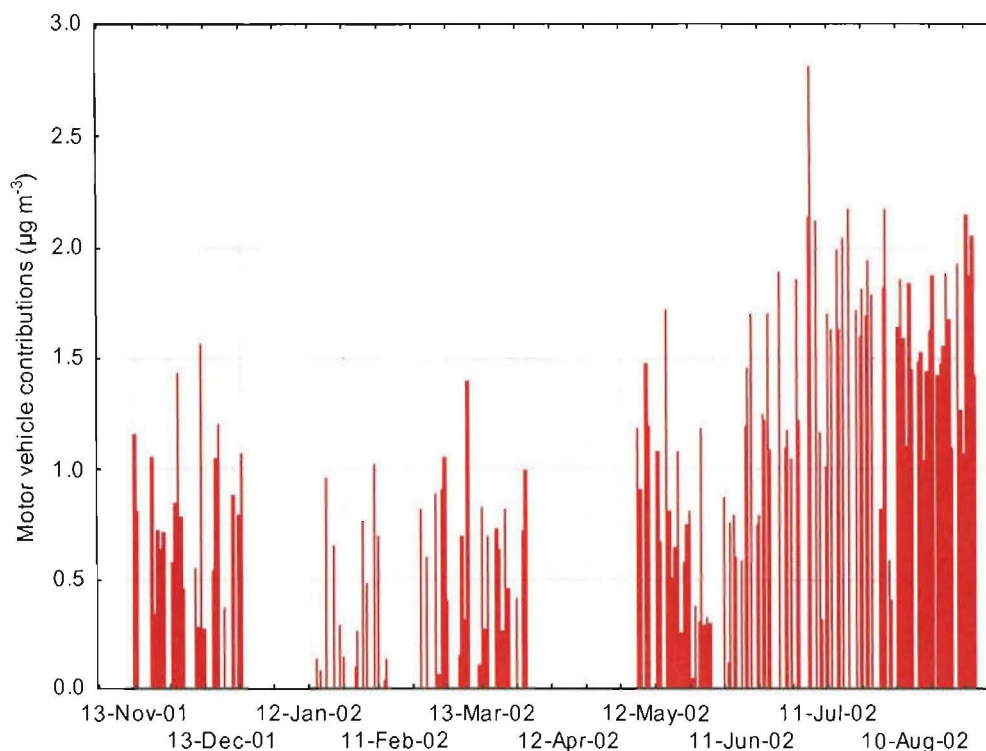


Figure 10.8 Daily motor vehicle contributions to PMF mass (24-hour averages), Christchurch, 2001/2002.

Figure 10.8 presents daily motor vehicle contributions to PMF mass. While a seasonal pattern is evident with lower contributions in summer, the relative difference between seasons is less pronounced than that for the wood combustion source. As indicated in Table 9.3, median motor vehicle contributions were $0.6 \mu\text{g m}^{-3}$ in the summer and $1.2 \mu\text{g m}^{-3}$ in the winter. Maximum contributions were $1.6 \mu\text{g m}^{-3}$ in the summer and $2.8 \mu\text{g m}^{-3}$ in the winter. The increased contribution in winter is related to variations in seasonal meteorology rather than changes in motor vehicle use in Christchurch. Figure 10.9 presents daily motor vehicle counts for the 2001/2002 sampling days on a major road located in St Albans. Daily variations are clearly evident but there is little difference in motor vehicle use on a seasonal basis. While meteorology is likely to be a key determinant of motor vehicle contributions, the apparent link with the aged aerosol source suggests that during the warmer months of the year, motor vehicle emissions may be partially responsible for aged aerosol. Likewise, motor vehicles are also most likely responsible for secondary particulate contributions as these are key sources of the secondary particulate precursor gases. This is discussed further in the ensuing sections.

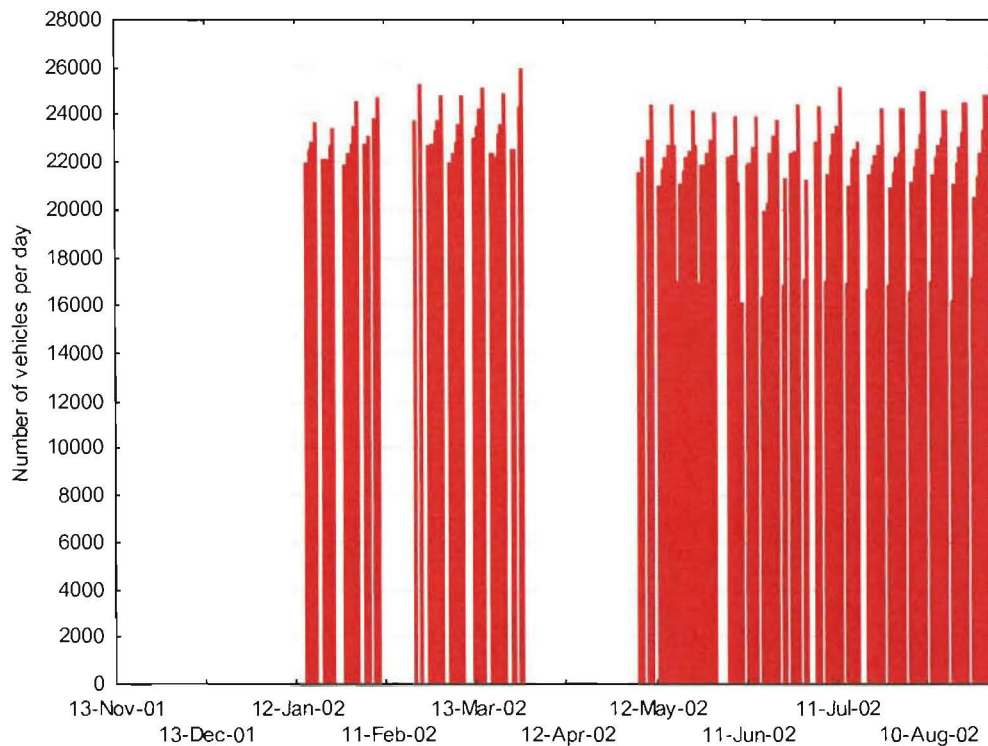


Figure 10.9 Daily motor vehicle counts recorded at the Transit Control Site, Cranford St, Christchurch (courtesy of Environment Canterbury).

10.2.3 Characteristics of the peak motor vehicle event

Review of the peak motor vehicle event - and the source contributions, elemental composition, particle characteristics, diurnal contaminant concentrations and meteorological conditions associated with them - assists in determining whether the source has been correctly identified in a physical sense. Intuitively, it would be expected that motor vehicle use would be greatest on cold winter days, and emissions most significant, when peak hour traffic coincides with temperature inversions and low wind speeds. Figure 10.10 presents hourly average motor vehicle counts on Cranford St in St Albans, approximately 0.4 km from the sampling site, during 2002. A small peak occurs in the morning between 8 and 9 am, with a slight decline in the following hour. Then a steady increase occurs throughout the day until traffic volumes peak at 5 pm. From 6 pm, vehicle numbers rapidly decline to low numbers overnight.

The five peak motor vehicle events, which occurred in July and August 2002, are listed in Table 10.4. Twenty-four hour average concentrations of SO_2 , NO, NO_2 , NO_x , CO, $\text{PM}_{2.5}$, PM_{10} (measured by a high volume sampler), and PMF mass is included, together with the motor vehicle contributions.

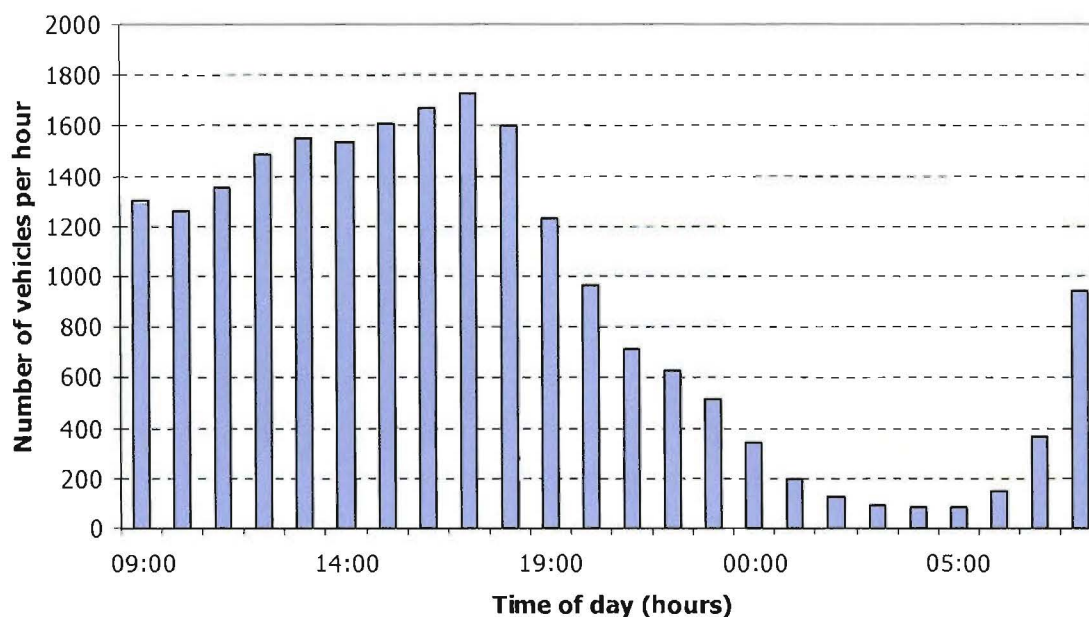


Figure 10.10 Motor vehicle counts recorded at the Transit Control Site, Cranford St, Christchurch (courtesy of Environment Canterbury).

Table 10.4 Five peak motor vehicle events, 24-hour average data, Christchurch, 2001/2002.⁵⁶

Date	SO ₂ ($\mu\text{g m}^{-3}$)	NO ($\mu\text{g m}^{-3}$)	NO ₂ ($\mu\text{g m}^{-3}$)	NO _x (ppb)	CO (mg m^{-3})	PM _{2.5} ($\mu\text{g m}^{-3}$)	PM ₁₀ Hivol ($\mu\text{g m}^{-3}$)	Motor vehicles ($\mu\text{g m}^{-3}$)	PMF mass ($\mu\text{g m}^{-3}$)
5/7/02	9	26	20	29	0.6	21	23	2.8	26
18/7/02	7	18	27	27	1	27	42	2.2	27
31/7/02	11	26	30	34	1	38	48	2.2	38
4/7/02	18	103	41	97	2.6	75	73	2.1	70
28/8/02	7	18	23	25	1	19	24	2.1	18

Estimated source contributions and key elemental constituents

The peak motor vehicle event occurred on 5 July 2002. Figure 10.11a and b presents the estimated source contributions, and the main elemental species present in PM_{2.5}, for that day. The PM_{2.5} concentration on 5 July 2002 was relatively low (21 $\mu\text{g m}^{-3}$) and PMF mass was slightly overestimated at 26 $\mu\text{g m}^{-3}$. Although the greatest contributions from this source occurred on this day (2.8 $\mu\text{g m}^{-3}$), motor vehicles only contributed to 11% of total PMF mass. The most significant source was wood combustion (72%) followed by secondary particulate (14%). Minor contributions were also made by aged (2%) and marine aerosol (1%). The main elemental species were TC_{mass} (89%), nitrate (4%), ammonium (2%), sulphur (1%), chlorine (1%), silicon (1%), potassium (1%) and sodium (1%).

⁵⁶ Data presented in Table 10.4 indicate that PM_{2.5} exceeds PM₁₀ on one of the five days. However, examination of the data records did not provide any justification for invalidating the data and it is assumed that the difference is related to variations in the instruments used to collect the samples. PMF mass was greater than PM_{2.5} on 5 July 2002, but some variation from observed data is expected in model results.

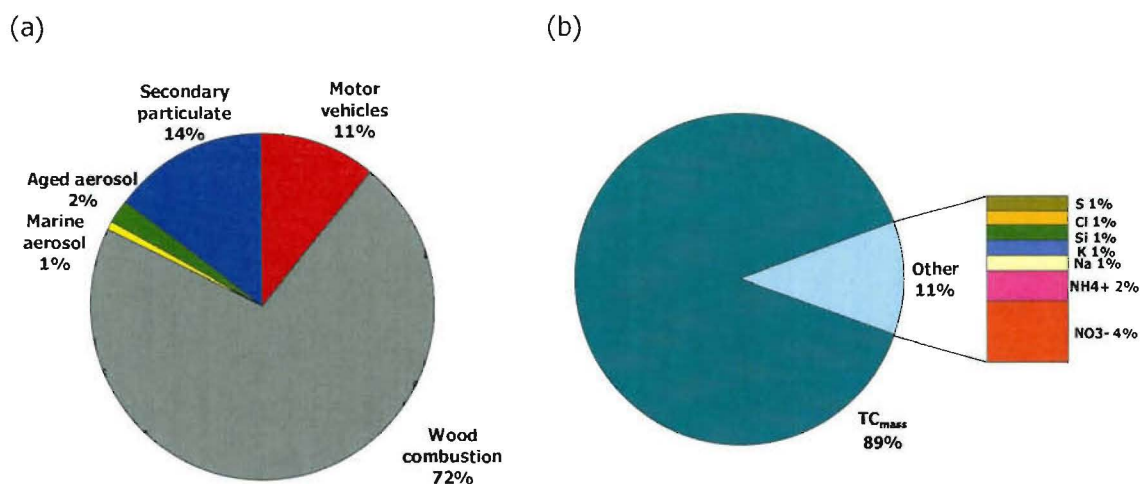


Figure 10.11 Contributions to (a) PMF mass and (b) to the sum of the PM_{2.5} constituents on 5 July 2002, Christchurch.

Particle characteristics

Unfortunately, SEM micrographs were not available for 5 July 2002. However, owing to the dominance of wood smoke particles on the filter, it would have been difficult to differentiate between particles of motor vehicle and wood smoke origin. Micrographs of motor vehicle PM are available in the literature and several of these are included (Figure 10.12a to d) for illustrative purposes. Figure 10.12 show particles produced from the combustion of petrol (a) and diesel (b), as combusted in a laboratory (i.e. they do not represent emissions discharged from in-use motor vehicles). Figure 10.12c presents emissions from a diesel truck aggregate sample (collected in-situ) and (d) directly from a diesel engine. These figures demonstrate that both petrol and diesel emissions contain particles that form branched, carbonaceous, spherule clusters. The morphology is not dissimilar to that observed in wood combustion emissions (e.g. Figure 10.5b; Murr and Bang, 2003), confirming the difficulty in differentiating between combustion-derived PM on a mixed source emissions filter, on the basis of particle structure alone.

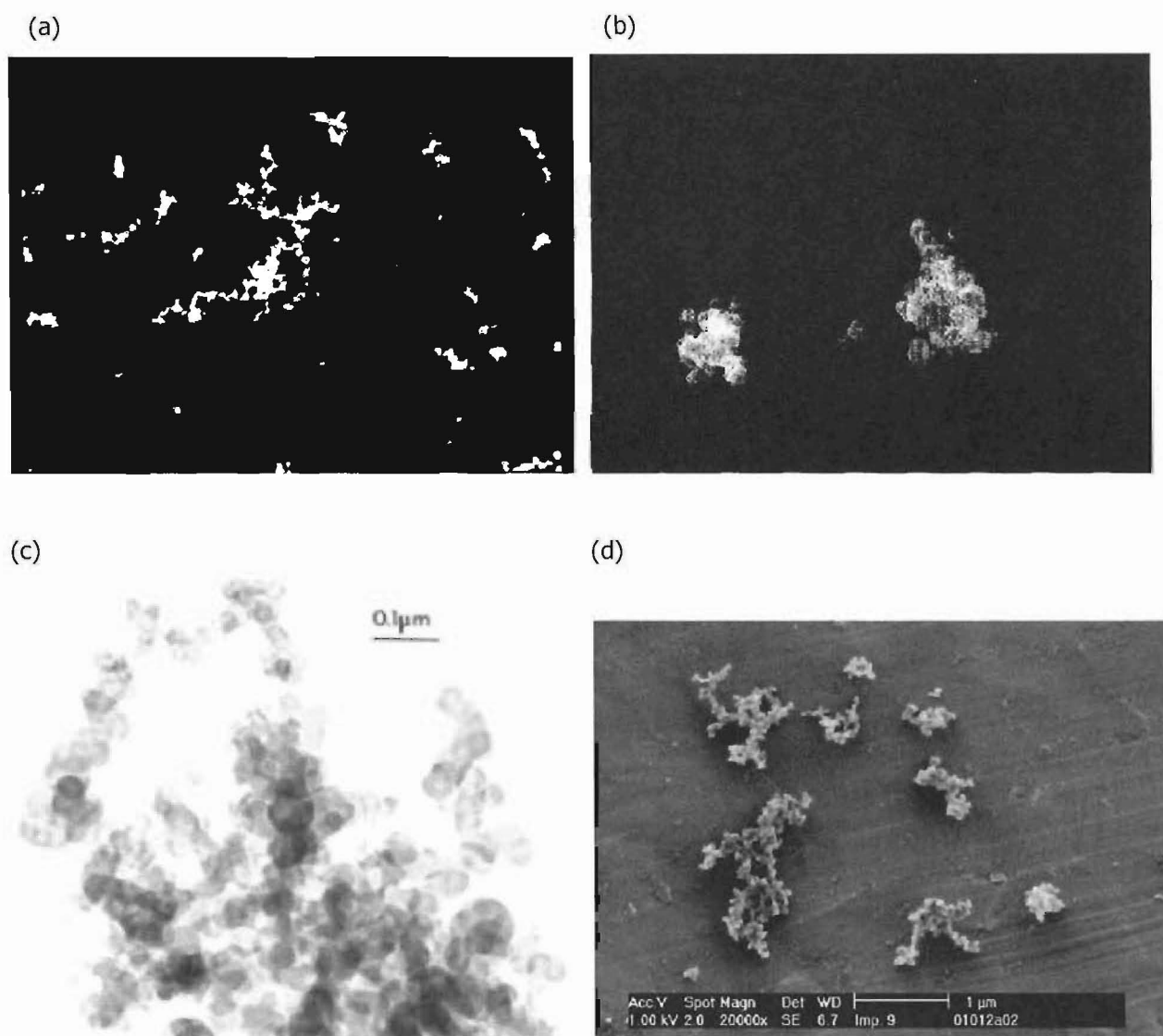


Figure 10.12 Particles discharged during the combustion of (a) petrol and (b) diesel, Colbeck *et al.* (1997), (c) in-situ diesel truck aggregate, Murr and Bang (2003), and (d) diesel engine emissions, Van Gulijk *et al.* (2004).

Temporal variations in meteorology and contaminant concentrations

Figure 10.13a to d presents hourly averaged contaminant concentrations (including PM_{10} measured by TEOM, SO_2 , NO, NO_2 , NO_x and CO), temperature difference, wind speed and direction, ambient temperature and relative humidity measured at Coles Place, St Albans, on 5 July 2002.

At 11 am, a morning peak in PM_{10} was evident with an hourly maximum concentration of approximately $35 \mu g m^{-3}$. PM_{10} concentrations decreased throughout the day and the minimum daytime concentration occurred at 1 pm. Temperatures were cool over the 24-hour period, with a maximum of $11^\circ C$ and a minimum of $2^\circ C$. A short-duration temperature inversion occurred from 4 pm to 7 pm, coinciding with overnight peaks in hourly PM_{10} , NO and NO_x concentrations. The NO and NO_x peaks were not insignificant at $240 \mu g m^{-3}$ and 200 ppb, respectively, despite the low 24-hour averages. Light winds blew throughout the day tending southwesterly to northeasterly, and stronger

northeasterlies dominated overnight. The timing of the inversion appears to be the most crucial feature of the meteorology, as it corresponded with those hours when most people were travelling home from work (Figure 10.10). Low wind speeds were also important.

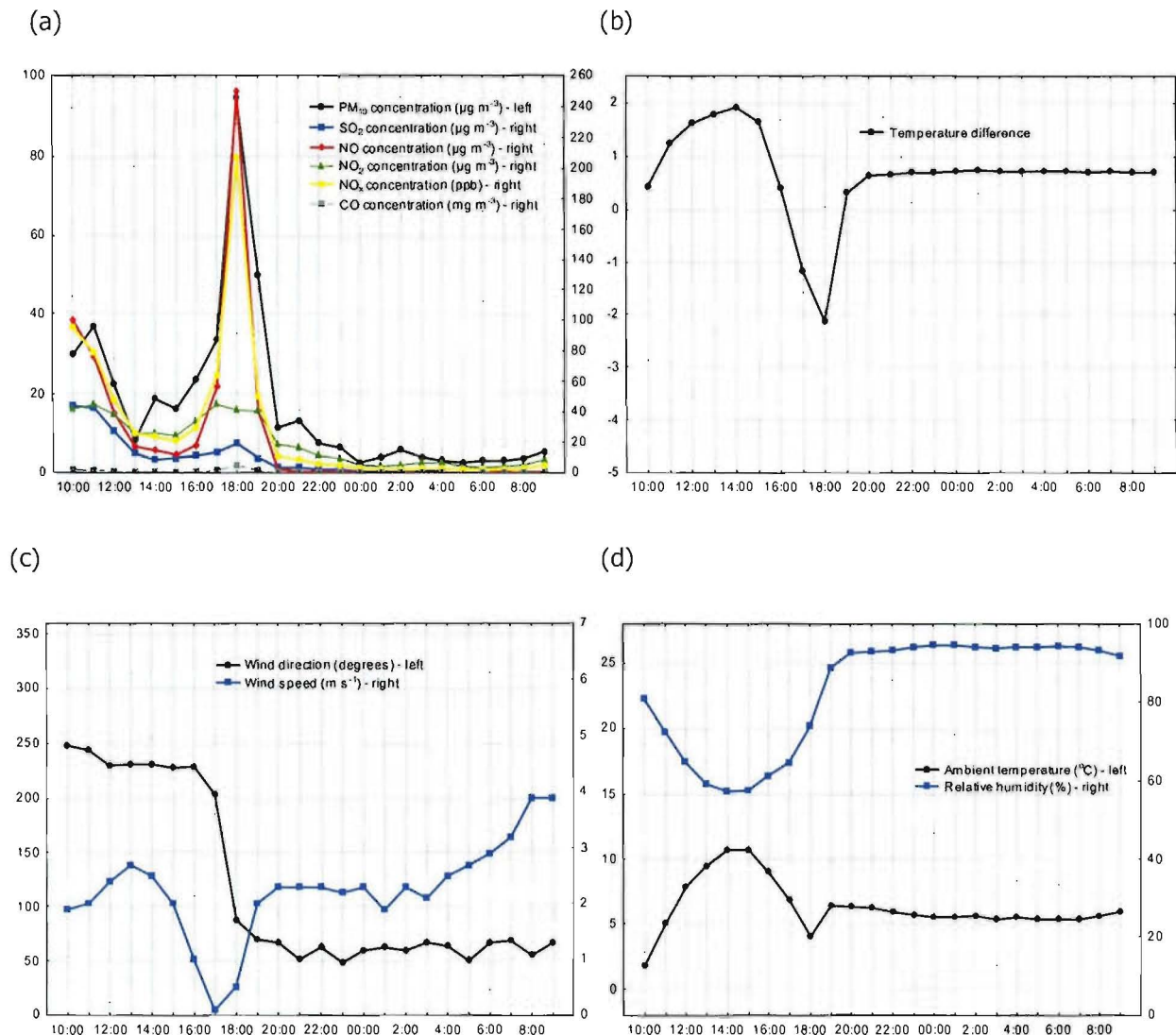


Figure 10.13 Contaminant and meteorological data for 5 July 2002, St Albans, Christchurch.

Appendix 3 presents a matrix plot of sources and various meteorological variables including wind speed, temperature and relative humidity. The motor vehicle scatter plots suggest that motor vehicle contributions were greatest at a variety of wind speeds, but mostly at the lower end. Likewise, the contributions were highest when temperatures were low, although a cluster of data points indicate that low motor vehicle contributions also occurred at low temperatures. Also, higher contributions occurred when relative humidity was high. The correlations between motor vehicle contributions and the meteorological variables, however, are weak as indicated in Appendix 4. The most significant association was that between motor vehicles and aged aerosol (-0.52) in both summer and winter.

The nature of this apparent link is unclear but it may simply be due to the correlation of nitrate, present in the motor vehicle profile but absent from the aged aerosol profile, with temperature. The highest nitrate concentrations (and the motor vehicle contributions) occurred at low temperatures, but aged aerosol was more significant at higher temperatures.

Attached in Appendix 6 are the diurnal profiles of PM_{10} concentrations and temperature difference for the remaining four events indicated in Table 10.4. Peaks in PM_{10} are evident on all days but the maximum concentrations vary from 65 to $210 \mu g m^{-3}$. Although the pattern is variable, PM_{10} peaks either coincided with peak traffic times (i.e. between 8 to 10 am and 4 to 6 pm) or had morning peaks that were as prominent as, and sometimes greater than, the overnight peaks. These also tended to coincide with the presence of a temperature inversion.

The elemental profile, diurnal contaminant pattern and meteorology support the identification of this factor as a motor vehicle source. However, high motor vehicle contributions would also be expected on peak $PM_{2.5}$ days, when conditions such as strong temperature inversions and low wind speeds occurred. Peak motor vehicle contributions (Table 10.4) did not coincide with the five highest $PM_{2.5}$ days (15, 22 and 30 May 2002, 8 and 9 July 2002); motor vehicle contributions were relatively low on those days. While it is uncertain exactly why this was the case, there are a number of possible explanations for this finding.

It may be that on high $PM_{2.5}$ days, the influence of meteorology on daily PM is greater than variations in source emissions. If so, this would contravene one of the primary receptor modelling requirements (Section 4.2), where the effect of processes such as temperature inversions on all emissions must be less than processes that affect individual sources (Seinfeld and Pandis, 1998). On these days, it may be more difficult to adequately separate out minor source contributions from those of the more dominant PM sources.

Alternatively, under strong temperature inversion conditions, roadside emissions may not remain in the atmosphere as long as that of PM discharged at greater heights above ground level. Particles discharged at a height of 5 m, such as from a residential chimney, could potentially remain airborne for longer periods of time than that discharged at ground level. Localised effects have been demonstrated previously in Christchurch, where CO concentrations substantially decreased with increasing distance from the road (e.g. Gunatilaka, 2002). Although CO is a gas, motor vehicle particulate emissions could behave in a similar manner, thus limiting impacts to roadside locations. However, such an effect has yet to be reported.

The most likely cause of the relatively lower motor vehicle contributions on peak $PM_{2.5}$ days is that atmospheric chemical processes may have transformed motor vehicle emissions into secondary

particulate compounds and thus become associated with other sources. For example, on the peak $\text{PM}_{2.5}$ day (22 May 2002), ambient temperatures were warm (atypical of motor vehicle events), concentrations of sulphur ($1 \mu\text{g m}^{-3}$) and sodium ($1.2 \mu\text{g m}^{-3}$) were high, and aged aerosol contributions were relatively substantial ($3.5 \mu\text{g m}^{-3}$). This information suggests that under these warm, still conditions, photochemical transformation has led to the production of Na_2SO_4 . Although sulphur does not feature in the motor vehicle profile, there is a negative correlation between motor vehicles and aged aerosol (mostly Na_2SO_4). When aged aerosol contributions are high, motor vehicle contributions are low. This suggests a link between the two, and it could be that sulphur associated with diesel vehicle emissions reacts with NaCl to form aged aerosol under warm conditions. Similarly, photochemical processes appear to be important on 8 and 9 July 2002, when two of the highest secondary particulate contributions occurred (6.2 and $6.1 \mu\text{g m}^{-3}$). These were mainly associated with high TC_{mass} , sulphur and ammonium concentrations. Again, this suggests that emissions from motor vehicles are being transformed into other compounds and becoming associated with other sources. Atmospheric chemistry was also important on the 15th and 30th of May, when both aged aerosol and secondary particulate contributions were relatively high. It is probable therefore that motor vehicle contributions are not limited to those identified as the "motor vehicle source". As discussed in the ensuing sections, motor vehicles were most likely responsible for the majority of the secondary particulate contributions, and for a proportion of the aged aerosol contributions.

Nevertheless, the factor described here does appear to represent motor vehicles, but may not account for the entire motor vehicle contribution. Further work may be needed to allow more complete estimates of the motor vehicle contributions to be derived.

10.3 Marine aerosol

10.3.1 Chemical composition

Figure 10.14 presents the elemental profile identified as "marine aerosol". Key elemental species were chlorine (52% of mass), sodium (39%), magnesium (4%), nitrate (3%), and calcium (1%). The high proportion of sodium and chlorine was a key indicator of marine aerosol origin.

Table 10.5 outlines the elemental species found in sea water. These may be compared to the marine aerosol profile. If it is assumed that magnesium is the most stable and reliable elemental measurement of those presented,⁵⁷ and elemental ratios are calculated on this basis, then the ratios in sea water are 14:1 for Cl/Mg , 8:1 for Na/Mg , 0.3:1 for K/Mg , 0.3:1 for Ca/Mg , and 2.6:1 for S/Mg . However, the proportional abundances found in sea water are not exactly the same as those of marine aerosol owing to "enrichment" effects (Brimblecombe, 1996). Marine aerosol is formed from

⁵⁷ Chlorine and sodium are not the best species to use for the ratios as chlorine may be depleted through chemical reactions in the atmosphere and the sodium measurements are less reliable than some of the other elemental species (Seinfeld and Pandis, 1998; Wilton, 2003).

the surface layer of the sea where elemental species have become enriched. Excess sulphur/sulphate and chlorine deficits may also be evident in the marine aerosol in response to atmospheric chemical processes. For example, NaCl reacts with H_2SO_4 vapour to form Na_2SO_4 and HCl vapour and results in a chlorine deficit (Seinfeld and Pandis, 1998.). Nevertheless, despite these differences, the species should be similar and the relative abundances may indicate the photochemical “age” of the aerosol.

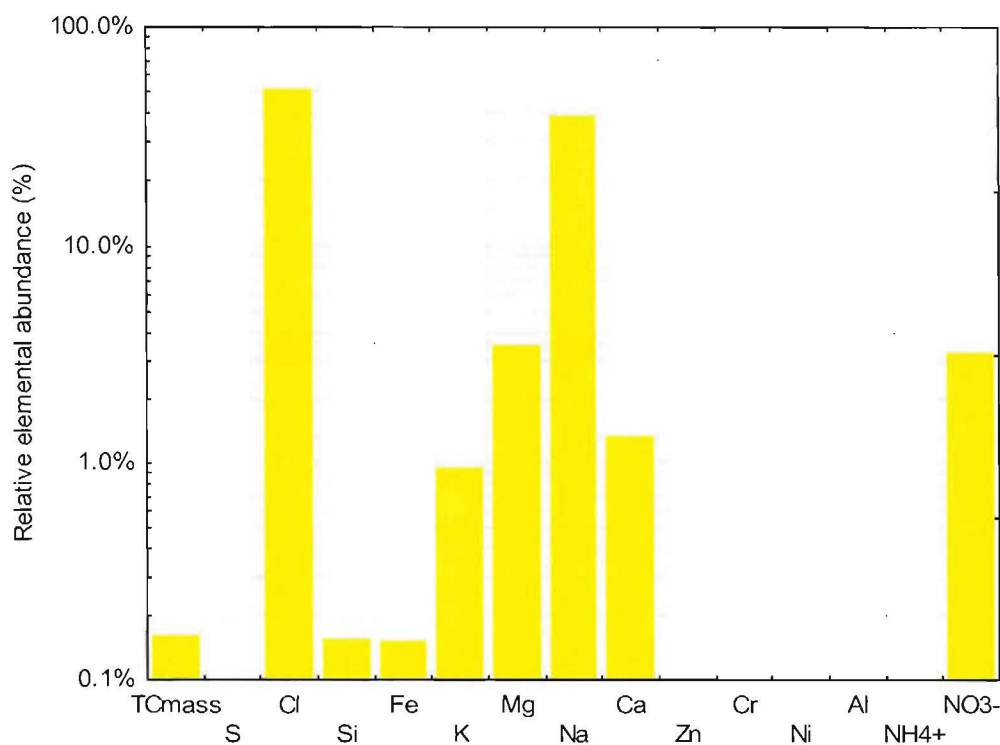


Figure 10.14 Marine aerosol profile, relative elemental abundance, Christchurch, 2001/2002.

Table 10.5 Chemical composition of sea water.

Sea water	g m^{-3}	%
Cl	19,000	54
Na	10,500	30
Mg	1,350	4
S	885	3
S as SO_4^{2-}	2,655	8
Ca	400	1
K	380	>1
Br	65	>1
Total	35,235	

Source: Stevenson (2002)

Table 10.6 presents the source profiles used to identify this factor including those derived from receptor modelling, measurements conducted in a seaside suburb of Christchurch (Sumner)⁵⁸ and source testing.

Table 10.6 Elemental profiles for marine aerosol sources (reference sources listed).

	OC	Na	Mg	Al	Si	S	Cl	K	Ca	Cr	Fe	Ni	Zn	NH ₄ ⁺	NO ₃ ⁻
Sumner, seaside suburb of Christchurch	NM	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓		
Other New Zealand profiles															
Wilson (1975)		✓	✓				✓	✓	✓						
Trompetter <i>et al.</i> (2000)		✓	✓				✓		✓						
Davy <i>et al.</i> (2002a)			✓				✓		✓						
Paterson (2002)		✓	✓				✓		✓						
International profiles															
Maykut <i>et al.</i> (2003)		✓					✓	✓	✓	✓					
Polissar <i>et al.</i> (1998)	EC	✓	✓			✓		✓	✓		✓				
Ramadan <i>et al.</i> (2000)		✓	✓		✓	✓	✓	✓			✓				
Polissar <i>et al.</i> (2001)	EC	✓	✓	✓	✓	✓	✓	✓	✓		✓		✓		
Song <i>et al.</i> (2001)		✓	✓			✓		✓	✓						✓
Speciate 3.2 database (USEPA)		✓	✓			✓	✓	✓	✓						
PMF marine aerosol	0.2%	39%	4%		0.2%		52%	0.9%	1%		0.1%				3%

NM = not measured

The main chemical constituents present in marine aerosol, as indicated in Table 10.6 were sodium, magnesium, chlorine, potassium and calcium. These were also evident in the factor identified as "marine aerosol" by this study. Small quantities of other elemental species were also found including carbon, silicon, iron and nitrate. These species were possibly derived from coastal combustion activities, and transported alongside the marine aerosol to the receptor at Coles Place. Elemental ratios relative to magnesium for this factor were 14:1 for Cl/Mg, 0.3:1 for K/Mg, 11:1 for Na/Mg and 0.3:1 for Ca/Mg. These were similar to those indicated for sea water, with the exception of sodium. The ratio of chlorine to magnesium, in particular, suggests that this comprises a relatively fresh, unreacted marine aerosol, sampled before significant photochemistry has had time to occur (i.e. likely to be of local origin). Notable differences in the ratios relative to sea water include the high sodium component and the absence of sulphur. It is uncertain why sodium is more abundant than expected, but it may be related to the higher errors associated with the sodium measurements. Sulphur,

⁵⁸ The Sumner measurements, which were obtained from Environment Canterbury, were not collected specifically for this study. A different instrument was used (a filter-based GENT sampler) and the measurements may contain elements from other sources as sampling was conducted several blocks from the beach.

conversely, is mainly present as sulphate in marine environments and thus may be associated with the secondary particulate factor, potentially leading to an underestimate of the marine aerosol contributions. Nevertheless, this is one of the strongest factors resolved by the modelling and clearly appears to be of marine aerosol origin.

10.3.2 Contributions to mass

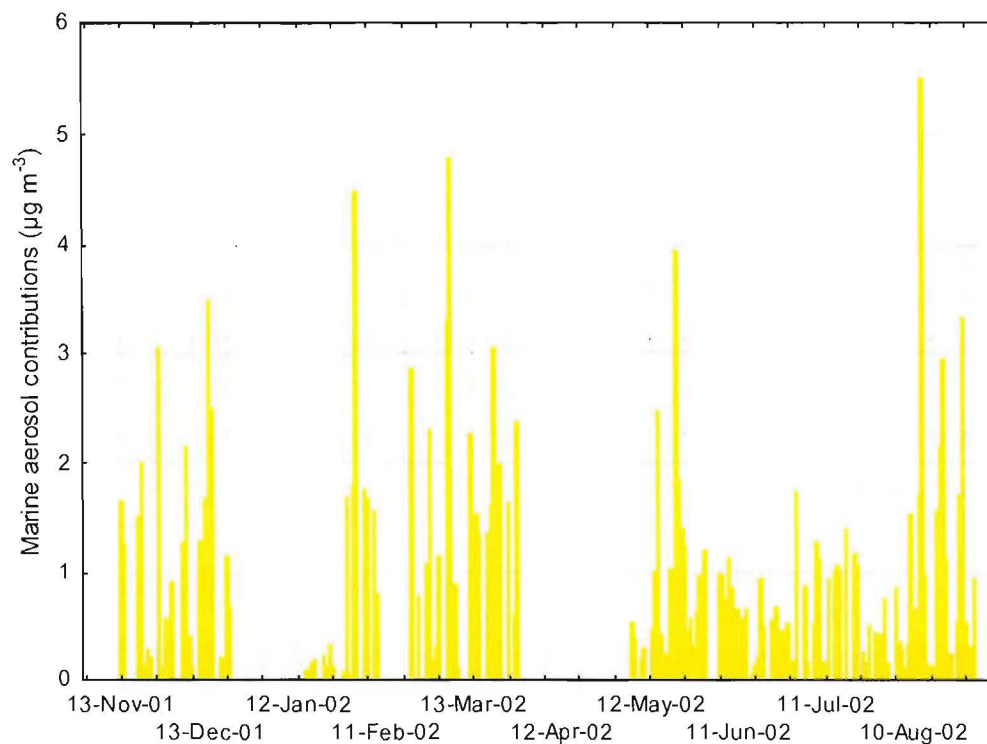


Figure 10.15 Daily marine aerosol contributions to PMF mass (24-hour averages), Christchurch, 2001/2002.

Figure 10.15 presents daily marine aerosol contributions to PMF mass. A seasonal pattern is evident with higher contributions in summer and lower contributions in winter. Peaks present at the beginning and end of winter correspond with slightly warmer, windier weather relative to the mid-winter period. In Christchurch, coastal sea breezes and elevated wind speeds are conducive to marine aerosol formation and transportation. These conditions are more prevalent outside the winter months. As indicated in Table 9.3, median marine aerosol contributions were $1.1 \mu\text{g m}^{-3}$ in the summer and $0.6 \mu\text{g m}^{-3}$ in the winter. Maximum contributions were $4.8 \mu\text{g m}^{-3}$ in the summer and $5.5 \mu\text{g m}^{-3}$ in the winter.

10.3.3 Characteristics of the peak marine aerosol event

Review of the peak marine aerosol event - and the source contributions, elemental composition, particle characteristics, diurnal contaminant concentrations and the meteorological conditions associated with it - assists in determining whether the source has been identified correctly on a physical basis. Marine aerosol contributions are likely to be greatest under persistent, northeasterly

sea breeze conditions and to occur during the summer months when these conditions are more prevalent. Data presented in Figure 10.15 demonstrate that most marine aerosol events occurred during the warmer months of the year, although two of the highest marine aerosol events occurred in the wintertime (albeit in early and late winter).

The five peak marine aerosol events are listed in Table 10.7. Twenty-four hour average concentrations of SO₂, NO, NO₂, NO_x, CO, PM_{2.5}, PM₁₀ (measured by a high volume sampler), and PMF mass are included, together with the marine aerosol contributions. There are two key features of interest in these numbers. First, the PM_{2.5} concentrations are low when marine aerosol events occur (less than 14 µg m⁻³). Second, PM_{2.5} comprises a lower proportion of PM₁₀ (27 to 75%) than that evident for combustion dominated events (e.g. wood combustion), suggesting a significant quantity of particles present on these days were in the coarse particle fraction (PM_{2.5-10}). This is consistent with what is commonly observed in the particle size distribution of marine aerosol constituents, where the greater numbers of particles are present in the smaller size fraction (i.e. less than 0.1 µm) but the bulk of the mass is evident as more coarse particles (i.e. between 1 and 10 µm; Morawska *et al.*, 1999; Colbeck, 1995).

Table 10.7 Five peak marine aerosol events, 24-hour average data, Christchurch, 2001/2002.

Date	SO ₂ (µg m ⁻³)	NO (µg m ⁻³)	NO ₂ (µg m ⁻³)	NO _x (ppb)	CO (mg m ⁻³)	PM _{2.5} (µg m ⁻³)	PM ₁₀ Hivol (µg m ⁻³)	Marine aerosol (µg m ⁻³)	PMF mass (µg m ⁻³)
13/8/02	6	2	12	8	0.2	14	27	5.5	19
5/3/02	4	-	-	-	0.3	10	20	4.8	9
1/2/02	0.9	3.2	11.3	7.9	0.2	7	26*	4.5	7
21/5/02	4.8	-	-	-	0.4	11	29	3.9	13
13/12/01	0	-	-	6.5	0.2	9	12	3.5	8

*This value comprises a TEOM at 40°C converted to a high volume sampler equivalent.

Estimated source contributions and key elemental constituents

The peak marine aerosol event occurred on 13 August 2002. Figure 10.16a and b presents the estimated source contributions, and the main elemental species present in PM_{2.5}, for that day.

The PM_{2.5} concentration on 13 August 2002 was relatively low (14 µg m⁻³) and PMF mass was slightly overestimated at 19 µg m⁻³. Although the greatest marine aerosol contribution occurred on this day (5.5 µg m⁻³), this source only contributed to 29% of total PMF mass. The most important source on this day was wood combustion (52%), with lower contributions from aged aerosol (10%), motor vehicles (6%) and secondary particulate (3%). The main elemental species were TC_{mass} (53%), sodium (17%), chlorine (18%), nitrate (3%), sulphur (3%), and magnesium (2%), with potassium, silicon and ammonium, each contributing to 1% of the measured constituent sum.

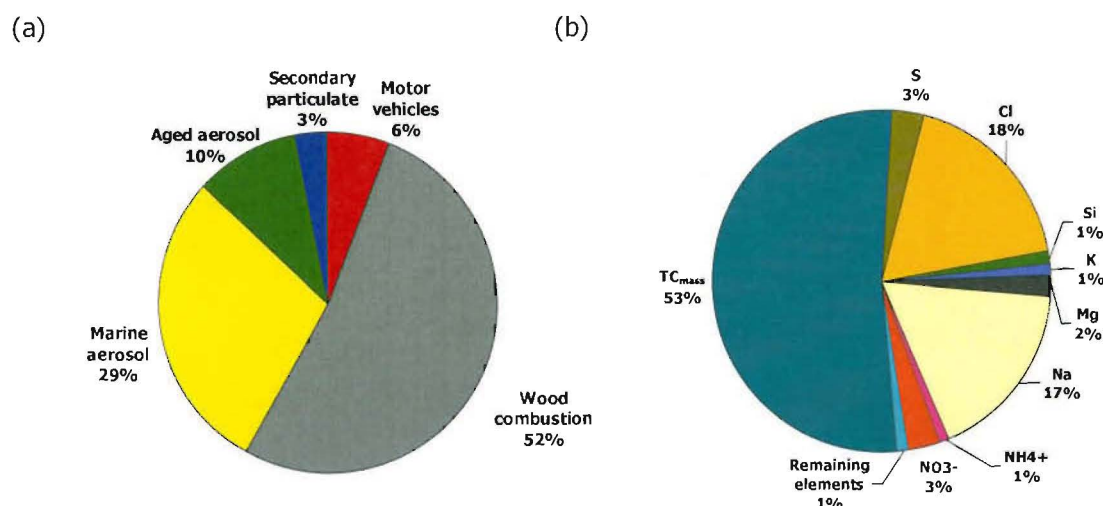


Figure 10.16 Contributions to (a) PMF mass and (b) to the sum of the PM_{2.5} constituents of PM_{2.5}, on 13 August 2002.

Particle characteristics

Figure 10.17 presents a selection of SEM micrographs of particles found on the filter of 13 August 2002. Figure 10.17a and b shows particles found on the daytime filter (approx 9 am to 10 pm), and c and d on the overnight filter (approx 10 pm to 9 am). Figure 10.17a and c are at the same resolution (x5,500), with Figure 10.17b and d at higher resolutions (x22,000 and x6,500 respectively). Figure 10.17a indicates that several types of particles were evident during the day including large salt crystals (as marked), chain-like agglomerates (bottom half of the figure) and a dense cluster located at the bottom right. A closer image (Figure 10.17b) shows a distinct NaCl particle (as identified by the elemental mapping program), and tightly-clustered carbon particles to the left. The broad nighttime filter image (Figure 10.17c) did not contain the same chain-like agglomerates as those found in the morning, but tighter agglomerates were present, as illustrated in Figure 10.17d. An EDS scan revealed that this particle was comprised of carbon, silicon and oxygen, suggesting that it may constitute a crustal particle (e.g. suggested by the presence of silicon); over-lain with combustion-derived PM. Overall, these filters support the findings of the modelling, that both combustion and marine aerosol particles were present on that day.

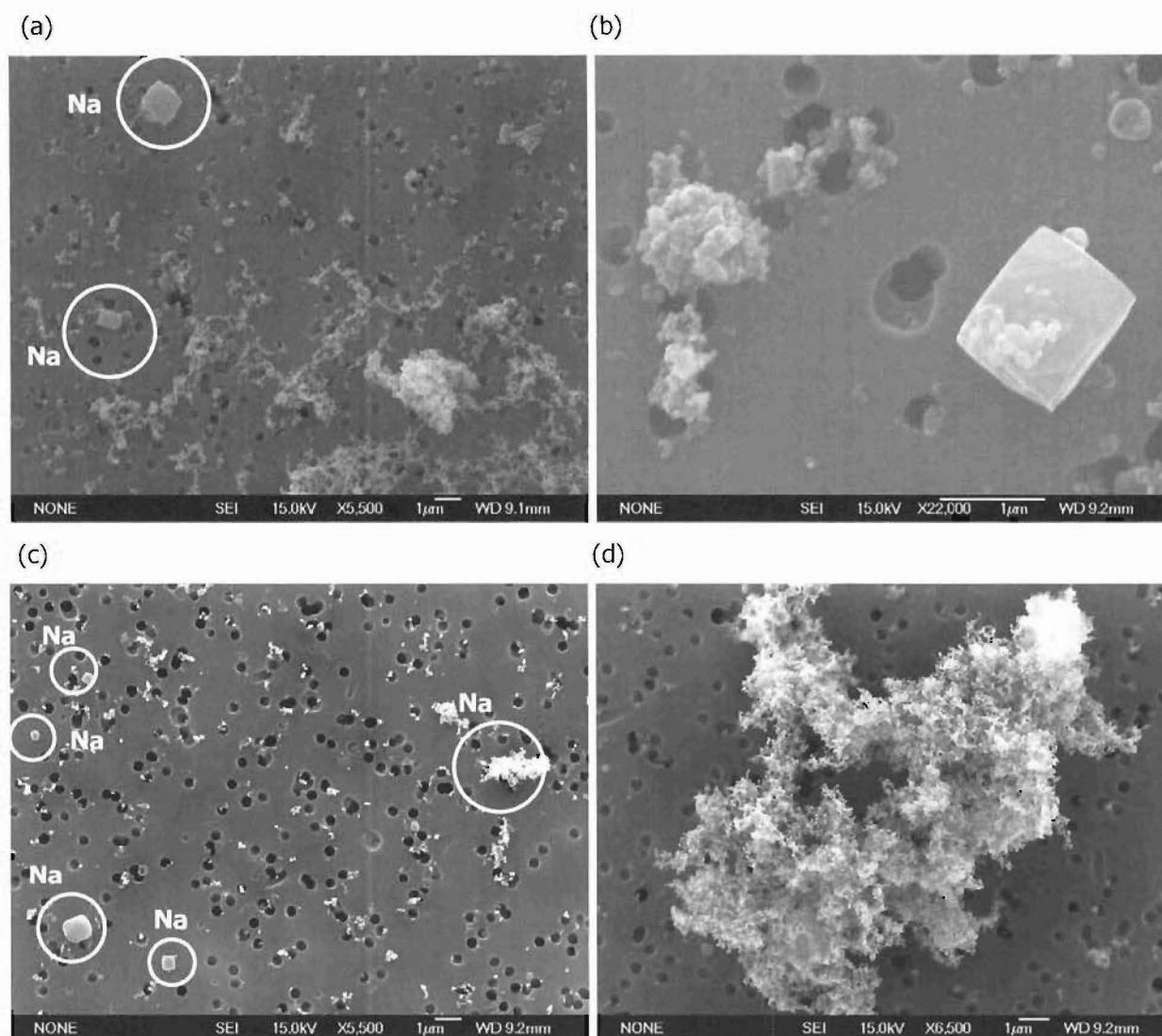


Figure 10.17 Particles sampled onto a polycarbonates filter on 13 August 2002 (NB: the elemental species indicated were identified by the elemental mapping software used).

Temporal variations in meteorology and contaminant concentrations

Figure 10.18a to d presents hourly average contaminant concentrations (including PM_{10} measured by TEOM, NO , NO_2 , NO_x , SO_2 and CO), temperature difference, wind speed and direction, ambient temperature, and relative humidity measured at Coles Place, St Albans on 13 August 2002.

At 10 am on 13 August 2002, wind speeds were approximately 6 m s^{-1} and from an easterly direction. Easterlies were predominant throughout the day and reasonably strong into the early evening period (5 pm to 9 pm). The winds were more northerly in aspect overnight, but tending easterly again the following morning. The wind strength varied with the strongest winds evident from the east. Relatively low particle concentrations were present in the morning and increased up to $45 \mu\text{g m}^{-3}$ during the day. Temperatures did not vary significantly during the daytime period, suggesting cloudy

and overcast conditions, and with relative humidity at greater than 85% (during the day).⁵⁹ As the wind changed to a northerly, ambient temperatures decreased, a temperature inversion developed (at midnight), and PM₁₀ concentrations decreased. Overall, meteorology did not vary significantly throughout the day, although wind speeds decreased on occasion and were more northerly in direction.

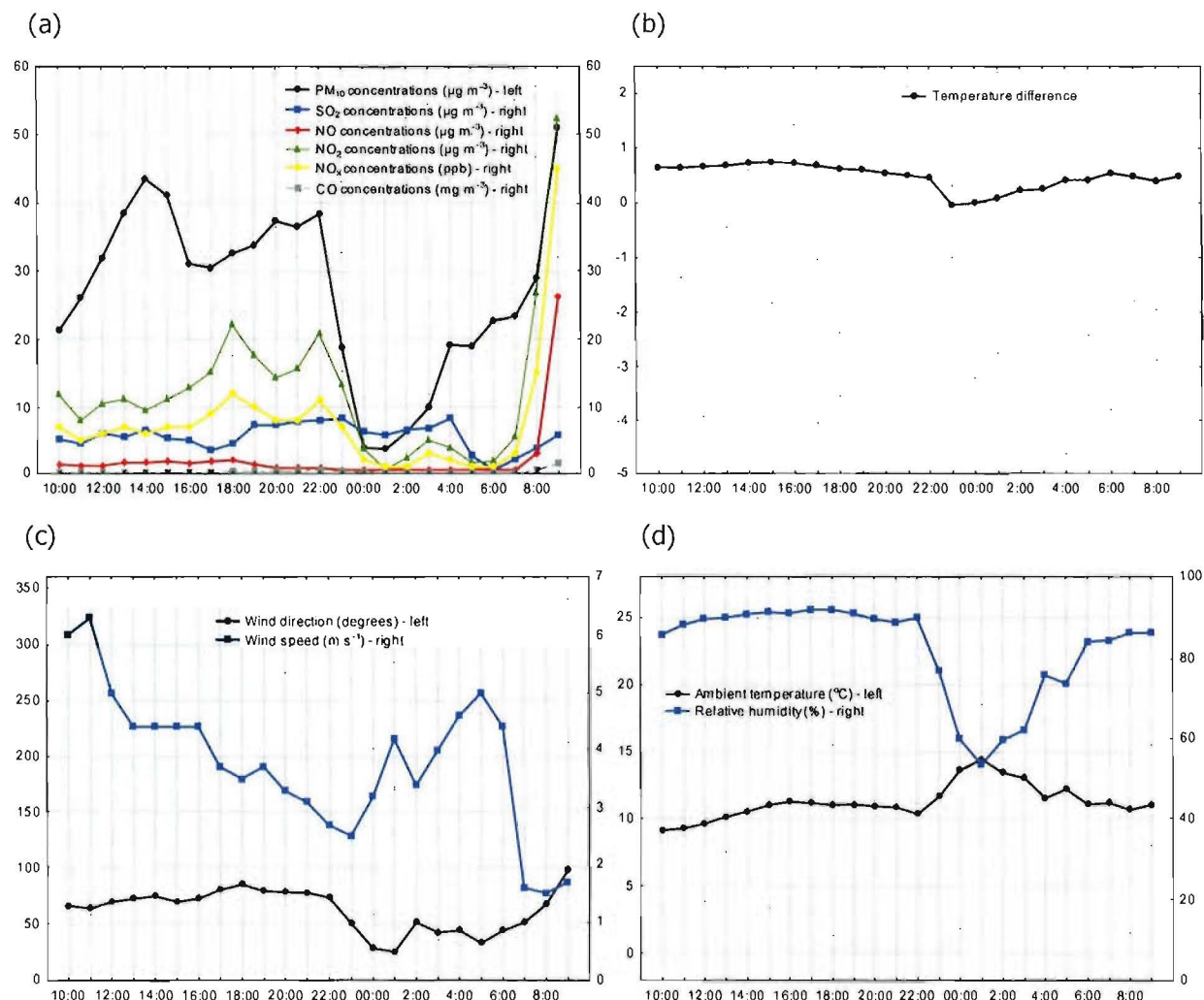


Figure 10.18 Contaminant and meteorological data for 13 August 2002, St Albans, Christchurch.

Appendix 3 presents a matrix plot of sources and various meteorological variables including wind speed, temperature and relative humidity. The scatter plots for marine aerosol suggest that contributions from this source were high at greater wind speeds, and occurred at a variety of temperatures and relative humidity. The correlation analysis presented in Appendix 4 also suggests that the strongest associations between sources and meteorological variables occur in the summer months. There appeared to be a negative correlation with secondary particulate (-0.47)⁶⁰ and a weak

⁵⁹ Environment Canterbury rain gauge data did not detect any significant moisture on this day so it was unlikely that there was drizzle or rain present.

⁶⁰ Wind speed was more likely to be responsible for the link between the two sources. Secondary particulate occurs under low wind speed conditions, whereas marine aerosol is associated with higher wind speeds.

positive correlation with wind speed (0.4). Wind direction and speed were the key meteorological influences on marine aerosol concentrations and the diurnal profiles of these variables for the remaining four events indicated in Table 10.7 are included at Appendix 7. All events were characterised by elevated daytime wind speeds. Wind direction was more variable with only two of the events typified by easterly sea breezes - the other two occurred under southwest or westerly conditions. Possibly, marine aerosol measured on those days has been transported from elsewhere (i.e. from south of Banks Peninsula).

Nevertheless, the presence of key elemental species, a greater proportion of coarse particles, and the incidence of relatively strong northeasterly sea breezes supports the identification of this factor as a marine aerosol source.

10.4 Secondary particulate

10.4.1 Chemical composition

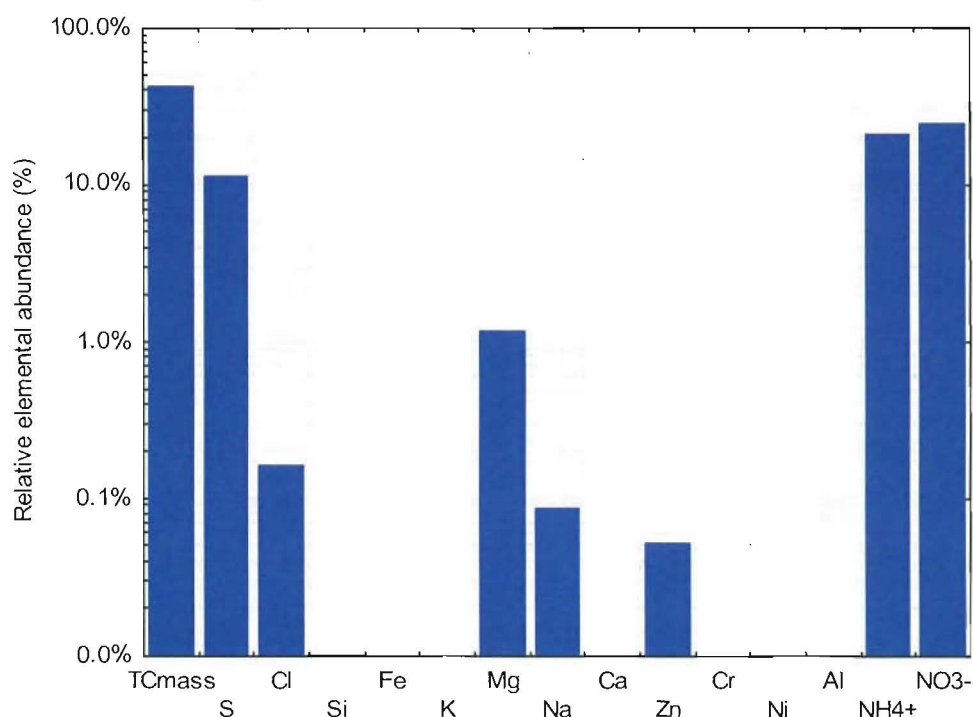


Figure 10.19 Secondary particulate profile, relative elemental abundance, Christchurch, 2001/2002.

Figure 10.19 presents the elemental profile of the factor identified as “secondary particulate”. Key elemental species were TC_{mass} (42% of mass), nitrate (25%), ammonium (21%), and sulphur (11%). While the high proportion of carbon was suggestive of a combustion source, the relative abundance of nitrate and ammonium indicates that it was more likely to be a secondary particulate source. Sulphur and carbon can be present in atmospheric particles in both primary and secondary forms where sulphur is present as sulphate, and OC as a wide variety of organics including aromatic

hydrocarbons. EC may also be present in secondary particulate profiles, as it plays a role in the oxidation of SO₂ to sulphate. Sulphate is soluble and requires an EC core for it to remain in the atmosphere (Chow, 2003). In addition, Liu *et al.* (2005) indicate that secondary aerosols are often associated with carbon and tracer elements and that this association is consistent with other studies in the eastern USA (Song *et al.*, 2001; Kim and Hopke, 2003; Kim *et al.*, 2003b). Also present in the profile were very small quantities of chemical species normally found in marine aerosol (sodium, chlorine, magnesium and calcium).

The main compounds associated with secondary particulate are (NH₄)₂SO₄, NH₄HSO₄, H₂SO₄, Na₂SO₄, NH₄NO₃, and NaNO₃ (Chow and Watson, 1998). As PMF provides factors in real units, it is possible to review the ratios of the species in the source profiles to determine whether the factor represents a particular secondary species or a mixture of compounds. A ratio of 1.1:1 is expected for (NH₄)₂SO₄ (based on a ratio of NH₄⁺ to S), 0.6:1 for NH₄HSO₄ (ratio of NH₄⁺ to S), and 0.3:1 for NH₄NO₃ (ratio of NH₄ to NO₃). The species present in this factor do not correspond with any of these ratios and it is assumed, therefore, that this factor represents a combination of secondary particulate species. Sodium was only present in very low quantities, thus it is unlikely that this source includes notable amounts of Na₂SO₄ and NaNO₃.

Table 10.8 outlines the range of receptor-modelled source profiles used to identify this factor. The profiles vary significantly from study to study, as some have resolved separate profiles for the different secondary particulate species. The species found are location-dependent, varying in response to climate and the availability of precursor species. Therefore, the profiles presented simply provide examples of secondary particulate profiles that may be resolved. Nevertheless, the key secondary constituents identified by these profiles include carbon (OC and EC), nitrate and sulphate.

Table 10.8 Elemental profiles for secondary particulate sources (reference sources listed).

	C	Na	Mg	Al	Si	S	Cl	K	Ca	Cr	Fe	Ni	Zn	NH ₄ ⁺	NO ₃ ⁻	SO ₄ ²⁻
Lewis <i>et al.</i> (2003)						✓										
Maykut <i>et al.</i> (2003)	EC														✓	✓
Kim and Hopke (2003) - sulphate I	✓				✓										✓	✓
Kim and Hopke (2003) - sulphate II	✓				✓			✓	✓						✓	✓
Kim and Hopke (2003) - sulphate III	✓	✓	✓													✓
Kim and Hopke (2003) - nitrate	OC	✓	✓	✓							✓		✓		✓	✓
Song <i>et al.</i> (2001) - nitrate	✓					✓		✓							✓	
Song <i>et al.</i> (2001) - sulphate	✓	✓			✓	✓									✓	
PMF secondary particulate	42%	0.1%	1%			11.2%	0.2%						0.1%	21%	25%	

10.4.2 Contributions to mass

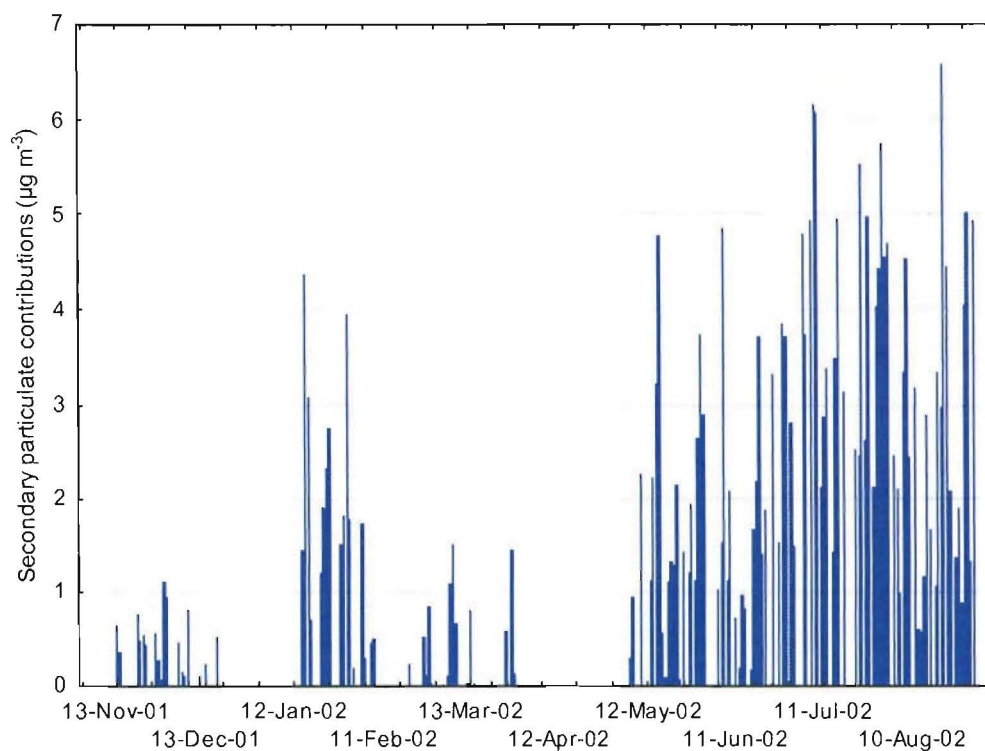


Figure 10.20 Daily secondary particulate contributions to PMF mass (24-hour averages), Christchurch, 2001/2002.

Figure 10.20 presents daily secondary particulate contributions to PMF mass. A seasonal pattern is evident with lower contributions in summer and higher contributions in winter. However, some notable peaks are also present in summer. As indicated in Table 9.3, median secondary particulate contributions were $0.4 \mu\text{g m}^{-3}$ in the summer and $2.2 \mu\text{g m}^{-3}$ in the winter. Maximum contributions were $4.4 \mu\text{g m}^{-3}$ in the summer and $6.6 \mu\text{g m}^{-3}$ in the winter.

Seasonal trends in secondary particulate source contributions were also reported by Song *et al.* (2001) and Kim and Hopke (2003), although these studies resolved separate nitrate and sulphate source profiles. These studies reported higher secondary sulphate contributions in the summer, and greatest secondary nitrate in winter. This is contrary to actual sulphate and nitrate concentrations measured by this study, with both nitrate and sulphate most abundant in the winter. Meteorology and greater accumulation of contaminants in winter may be the key factors leading to high wintertime secondary particulate concentrations in Christchurch.

10.4.3 Characteristics of the peak secondary particulate event

Review of the peak secondary particulate event – and the source contributions, elemental composition, particle characteristics, diurnal contaminant concentrations and the meteorological conditions associated with it – assists in determining whether the source has been identified correctly in a physical sense. The secondary particulate source was comprised of sulphates, ammonium and

nitrate, and while all three species are reliant on the mix of precursor emissions available for reaction, sulphates and nitrates tend to occur under different conditions. Sulphate frequently occurs under relatively warm, sunny conditions conducive to photochemical activity (e.g. Polissar *et al.*, 2001; Song *et al.* 2001), while nitrate is formed at low temperatures during nighttime hours (Meszaros, 1999).

The five peak secondary particulate events, which occurred in July and August 2002, are listed in Table 10.9. Twenty-four hour average concentrations of SO₂, NO, NO₂, NO_x, CO, PM_{2.5}, PM₁₀ (measured by a high volume sampler) and PMF mass are included, together with the secondary particulate contributions. The data presented in the table show that PM_{2.5} concentrations were variable under secondary particulate event conditions and comprised a substantial proportion of the PM₁₀ mass, ranging from 53% on 24 July 2002 to 99% on 9 July 2002. PMF mass was greater than PM_{2.5} on 8 July 2002 and 24 July 2002, but some variation is expected in model results, particularly at lower concentrations.

Table 10.9 Five peak secondary particulate events, 24-hour data, Christchurch, 2001/2002.

Date	SO ₂ (µg m ⁻³)	NO (µg m ⁻³)	NO ₂ (µg m ⁻³)	NO _x (ppb)	CO (mg m ⁻³)	PM _{2.5} (µg m ⁻³)	PM ₁₀ Hivol (µg m ⁻³)	Secondary particulate (µg m ⁻³)	PMF mass (µg m ⁻³)
21/8/02	12	69	39	70	3	54	60	6.6	53
8/7/02	13	116	37	105	3	69	89	6.2	87
9/7/02	13	85	29	78	3	95	96	6.1	89
31/7/02	11	26	30	34	1	39	48	5.7	38
24/7/02	8	8	25	18	1	15	28	5.5	25

Estimated source contributions and key elemental constituents

The peak secondary particulate event occurred on 21 August 2002. Figure 10.21a and b present the estimated source contributions, and the main elemental species present in PM_{2.5}, for that day.

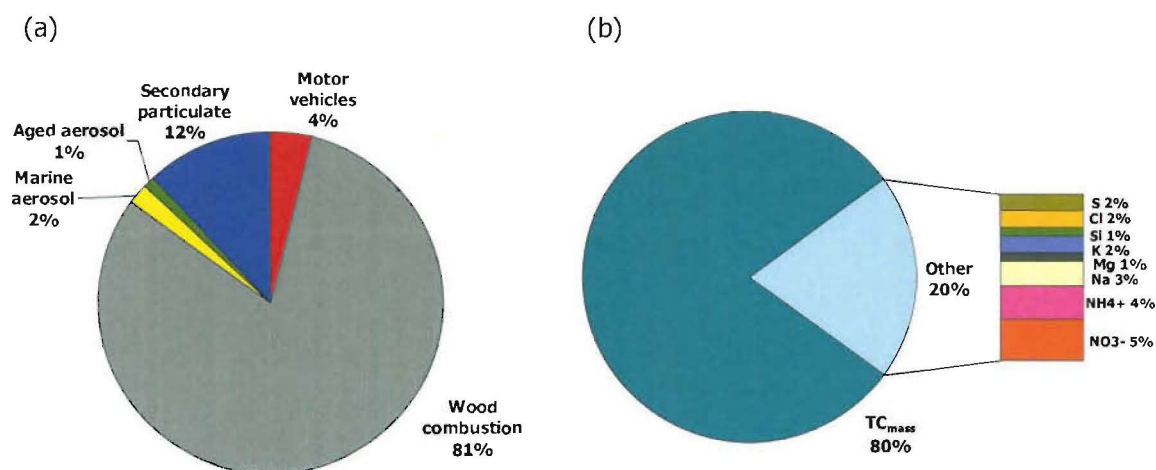


Figure 10.21 Contributions to (a) PMF mass and (b) to the sum of the PM_{2.5} constituents of PM_{2.5} on 21 August 2002, Christchurch.

The $\text{PM}_{2.5}$ concentration on 21 August 2002 was $54 \mu\text{g m}^{-3}$ and PMF mass was estimated at $53 \mu\text{g m}^{-3}$. Although the greatest secondary particulate contribution occurred on this day, this source only contributed to 12% of the total PMF mass. The most important source was wood combustion (81%), with lower contributions from motor vehicles (4%), marine aerosol (2%) and aged aerosol (1%). The main elemental species were TC_{mass} (80%), nitrate (5%), ammonium (4%) and sodium (3%).

Particle characteristics

Figure 10.22 shows a selection of SEM micrographs of particles found on the filter of 21 August 2002. Each image has a resolution of $\times 5,500$ thus providing a good indication of relative particle size. Figure 10.22a and b present particles found on the daytime filter (approximately 9 am to 10 pm), and Figure 10.22c and d on the overnight filter (approximately 10 pm to 9 am).

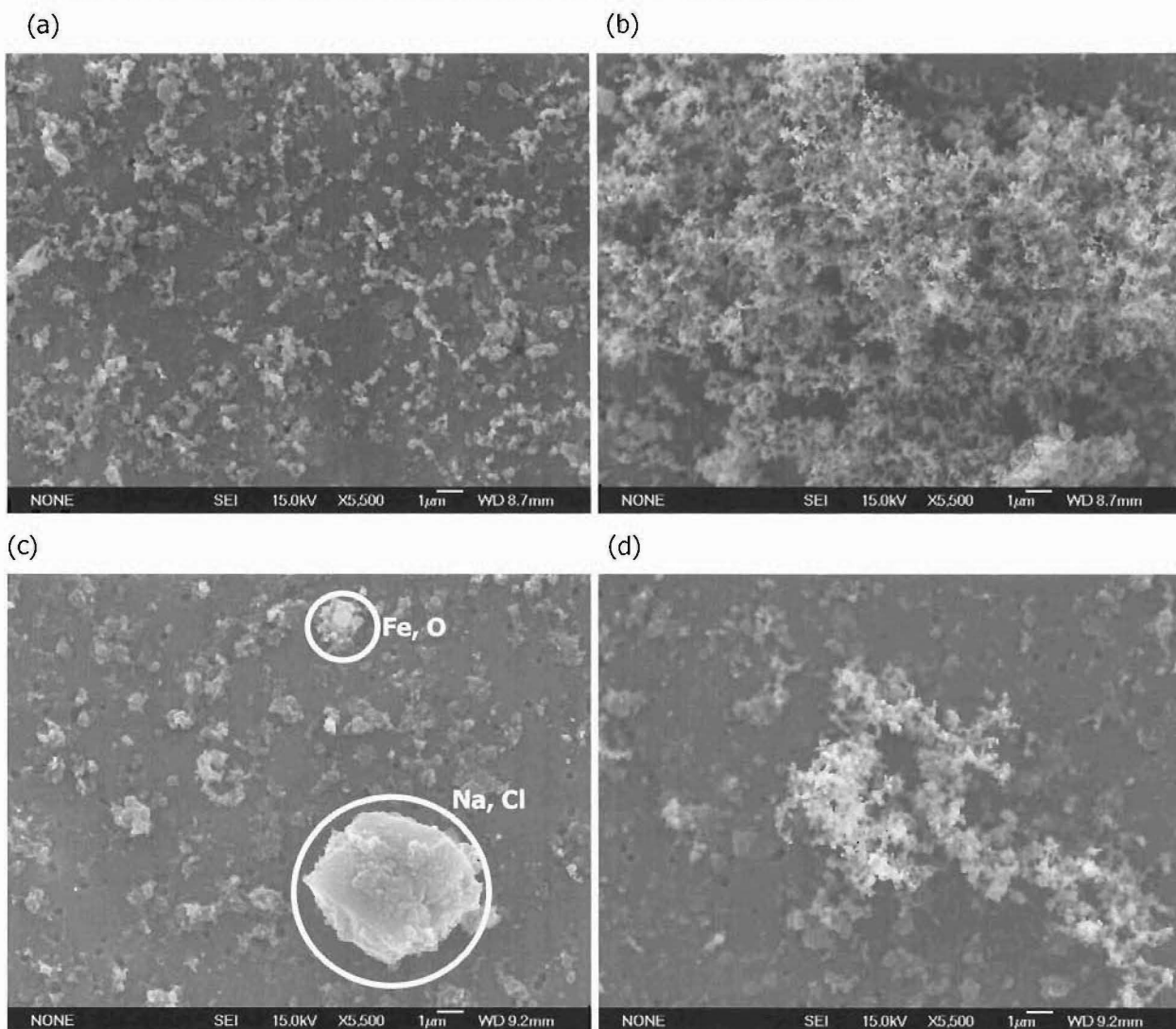


Figure 10.22 Particles sampled onto a polycarbonate filter on 21 August 2002 (NB: the elemental species indicated were identified by elemental mapping software).

Figure 10.22a shows a moderately loaded filter with a variety of small spherical particles, crystals and chain-like structures. Not all particles are small, however, as demonstrated by the very large particle in Figure 10.22b. It appears to be a large agglomerate made up of many tiny spherule chains. Elemental information was not available for this particle, although it may be assumed from its chain-like morphology that it is made up of carbon compounds and is of combustion origin. As the spherules are very small, this particle was probably formed from condensing vapours and increased in size through coagulation processes. The nighttime filters (Figure 10.22c and d) also show the presence of chain-like agglomerates and salt crystals. Figure 10.22c in particular, shows a high number of solid crystal particles. These smaller crystals may comprise NH_4NO_3 , as this compound takes on a crystalline form at lower temperatures. This is also supported by the chemical measurements where the highest ammonium concentration was measured on this day ($1.2 \mu\text{g m}^{-3}$), together with the fifth highest nitrate concentration ($1.6 \mu\text{g m}^{-3}$).

Temporal variations in meteorology and contaminant concentrations

Figure 10.23a to d presents hourly average contaminant concentrations (including PM_{10} measured by TEOM, NO , NO_2 , NO_x , SO_2 and CO), temperature difference, wind speed and direction, ambient temperature and relative humidity measured at Coles Place, St Albans on 21 August 2002.

Wind speeds were low throughout the day except for a period from 12 pm through to 8 pm when winds gradually increased and peaked at 2.6 m s^{-1} . The increase coincided with a change in wind direction from a northerly to a northeasterly direction. Apart from this period, the winds were generally of a northwesterly or northerly aspect and very light. Lower contaminant concentrations were evident during the day and increased overnight, with very high NO and NO_x concentrations occurring on the following morning, relative to the other contaminants. Temperatures were relatively warm during the day (up to 16°C), and relative humidity was low (25%). The temperatures dropped during the night, an inversion developed and relative humidity increased.

Appendix 3 presents a matrix plot of sources and various meteorological variables including wind speed, temperature and relative humidity. The scatter plots for secondary particulate suggest that contributions from this source were greatest at low wind speeds, higher temperatures and reasonably high relative humidity (but not in all cases). The correlation analysis presented in Appendix 4 also suggests that weak relationships were evident in both summer and winter months. In summer, weak associations occurred with marine aerosol (-0.47), aged aerosol (0.44) and relative humidity (0.4). This is not unexpected as marine aerosol occurs under different conditions (i.e. windier) to secondary particulate, whereas aged aerosol may occur under similar conditions due to its photochemical nature. Some association between secondary particulate and relative humidity was also expected, as moist air can lead to greater nitrate, sulphate and ammonium concentrations. In winter, weak associations occur with wood combustion (0.41), wind speed (-0.48) and temperature (-0.41). Wood combustion contributions are also greatest under low wind speeds and temperatures, so a co-linear

correlation with wood combustion is not unexpected. In addition, secondary particulate species such as nitrate, are preferentially formed at lower temperatures (Lee *et al.*, 2002b).

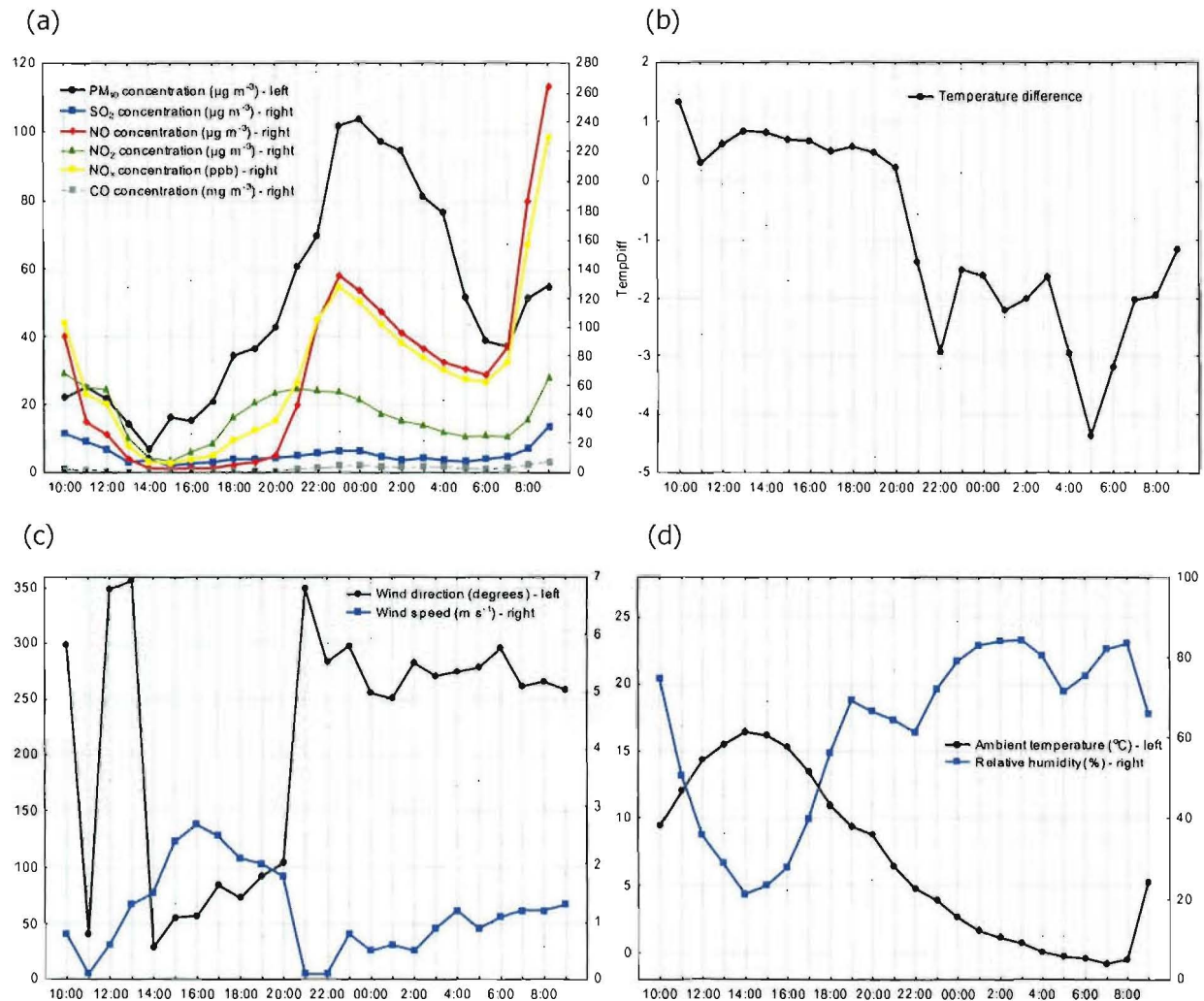


Figure 10.23 Contaminant and meteorological data for 21 August 2002, St Albans, Christchurch.

Wind speed and temperature were important contributing factors and these variables, together with wind direction and relative humidity, are presented in Appendix 8 for the remaining four events identified in Table 10.9. All events were characterised by low wind speeds (although these increased on occasion), winds from a northwesterly or northerly directions (some southwest winds were also evident), moderate daytime humidity (lows of 40 to 84%), and maximum temperatures greater than 10 $^{\circ}C$. In addition, NO and NO_x concentrations were relatively high during the morning periods with concentrations between 80 and 200 ($\mu g m^{-3}$ and ppb).

Widman and Presser (2002) outline key meteorological characteristics leading to secondary particulate formation. These include:

- Synoptic patterns and winds – to transport precursors into an area.
- Temperature – higher temperatures favour more reactive chemistry, although lower temperatures are more conducive to the formation of nitrates and for the condensation of some organic gases into the solid or liquid phases.
- Moisture – under conditions of high humidity and fog, the rate of particle formation may be greater leading to increased conversion of SO_2 to SO_4^{2-} .
- Vertical stability – leads to greater concentrations of precursor gases.

The conditions observed for this factor are consistent with those identified by Widman and Presser (2002), and are conducive to the accumulation of contaminants and the subsequent formation of secondary particulate compounds. The high nitrate, NO and NO_x concentrations on 21 August 2002, in particular, support NH_4NO_3 formation, which primarily occurs overnight and degrades during the day.

10.5 Aged aerosol

10.5.1 Chemical composition

Figure 10.24 presents the elemental profile identified as “aged aerosol”. Key elemental species were sulphur (44%), sodium (35%), silicon (7%), magnesium (5%), iron (2%), potassium (2%), calcium (2%), and aluminium (2%). The relative abundance of sodium and sulphur suggests that this factor may constitute an additional secondary particulate source, but one dominated by a single compound, Na_2SO_4 . As PMF provides factors in real units, it was possible to review the ratios of the species in the source profile to determine if this compound was the primary chemical constituent. Based on the relative molecular weight of Na to S in Na_2SO_4 a ratio of 1:1.4 is expected for this compound. However, the ratio of Na to S in this factor was 1:0.8, due to the high amount of sulphur present. This suggests that while Na_2SO_4 was likely to be the dominant species, there were other sulphur compounds present. A number of additional species were also found, several of which appeared to be of soil or marine aerosol origin (e.g. silicon, aluminium, chlorine and magnesium).

Table 10.10 outlines a range of receptor-modelled source profiles used to identify this factor. Several PMF studies identified a similar sulphur-type source to that found by this study and this was generally described as an aged aerosol. The elemental constituents of marine aerosol were found, with sodium and sulphur being the most dominant species. Chlorine was included in some profiles, but in most cases it had been depleted relative to sodium. These species were all present in this factor, suggesting that it was an aged or transported marine aerosol source that has undergone some chemical transformation. In particular, the abundance of sodium and sulphate (present as sulphur) indicated the presence of Na_2SO_4 .

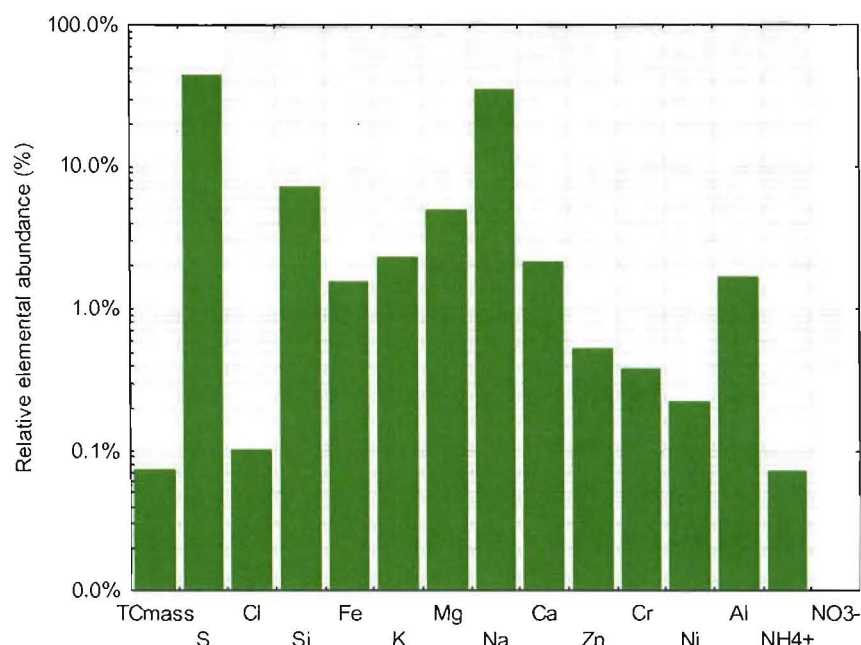


Figure 10.24 Aged aerosol profile, relative elemental abundance, Christchurch, 2001/2002.

The origin of the aged aerosol is uncertain. It could be aged marine air transported into Christchurch from elsewhere (mixed-down from aloft or contained within the sea breeze), or of local origin. Locally-derived contaminants could potentially be transported offshore late in the afternoon, react in the atmosphere with marine aerosol, and then be transported back onshore in the sea breeze later the following day. Similar processes were suggested by Lee *et al.* (2002b) for Brigantine in the US, where sea breezes transport marine aerosol overland and reactions with local SO₂ emissions occur, or local SO₂ emissions are transported offshore, react with marine aerosol and are transported back onshore in the sea breeze. However, other chemicals were also found in this factor, including soil species such as silicon, iron and aluminium. It is probable, therefore, that there is a long-range transport component to the factor where it has, at least in part, travelled overland. If so, soil and other sources have contributed to particle loadings in the air parcel as it is transported to Christchurch.

Table 10.10 Elemental profiles for aged aerosol sources (reference sources listed).

	C	Na	Mg	Al	Si	S	Cl	K	Ca	Cr	Fe	Ni	Zn	NO ₃ ⁻
Lee <i>et al.</i> (2002b) - aged sea salt		✓				✓	✓	✓	✓					✓
Kim <i>et al.</i> (2004b) - aged sea salt	✓	✓			✓	✓	✓	✓	✓		✓			✓
Zhao and Hopke (2004) - aged sea salt	✓	✓				✓		✓	✓					✓
Maykut <i>et al.</i> (2003) - Na-rich	✓	✓						✓	✓	✓			✓	✓
Polissar <i>et al.</i> (1998) - distant anthropogenic I	EC	✓	✓			✓		✓	✓		✓			
Polissar <i>et al.</i> (1998) - distant anthropogenic II	EC	✓			✓	✓		✓			✓			
Polissar <i>et al.</i> (2001) - Na-S	EC	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓		✓	
Kim and Hopke (2003) - aged sea salt	OC	✓	✓		✓	✓		✓	✓					✓
PMF aged aerosol	0.1%	35%	5%	2%	7.2%	44.1%	0.1%	2%	2.1%	0.4%	1.5%	0.2%	0.5%	

10.5.2 Contributions to mass

Figure 10.25 presents daily aged aerosol contributions to PMF mass. This is the only source that does not exhibit a distinct seasonal trend. As indicated in Table 9.3, median aged aerosol contributions were $1.7 \mu\text{g m}^{-3}$ in the summer and $1.4 \mu\text{g m}^{-3}$ in the winter. Maximum contributions were $4.2 \mu\text{g m}^{-3}$ in the summer and $3.8 \mu\text{g m}^{-3}$ in the winter.

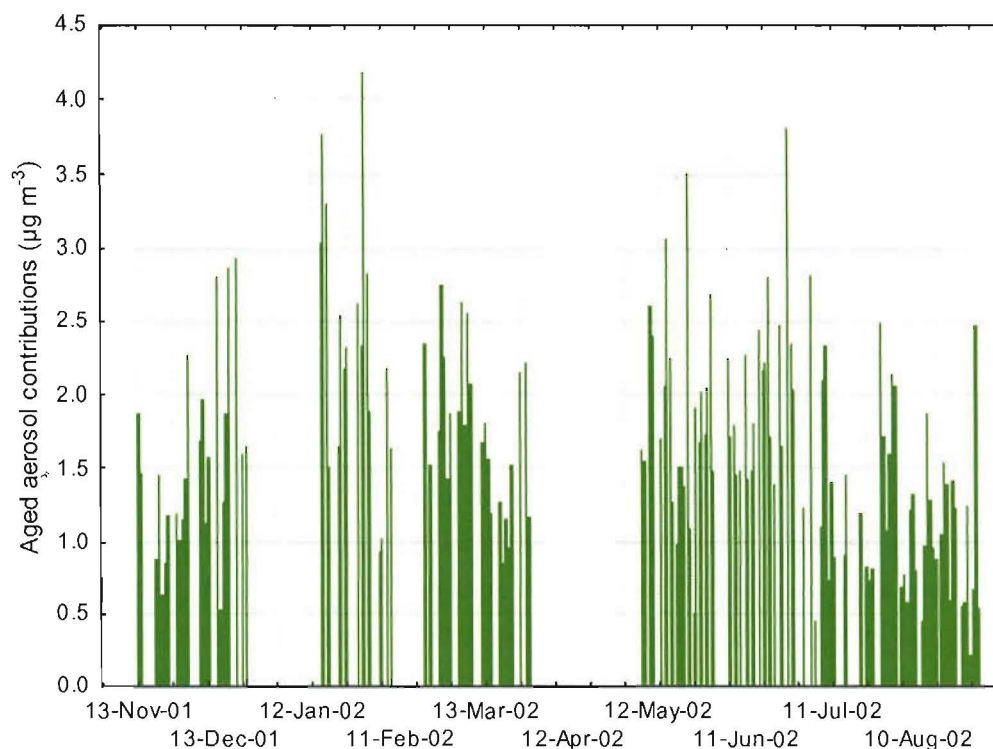


Figure 10.25 Daily aged aerosol contributions to PMF mass (24-hour averages), Christchurch, 2001/2002.

10.5.3 Characteristics of the peak aged aerosol event

Review of the peak aged aerosol event assists in determining whether the source identification makes physical sense. The conditions likely to lead to aged aerosol contributions in Christchurch are difficult to define, as the origin of the aged aerosol is unknown. If it is locally-derived then it would most likely be associated with land/sea breezes and thus primarily occur in summer, when these are more frequent. However, if transported overland it may be associated with westerly winds. Warmer temperatures and low wind speeds could also be expected, as these provide optimal photochemical conditions (i.e. sufficient sunlight and reaction time). In Alaska and Vermont USA, aged aerosol was greatest in the winter and spring months, and lowest in summer (Polissar *et al.*, 1998; 2001). However, the meteorology could be quite different to that of Christchurch, where a similar pattern would not necessarily be observed.

The five peak aged aerosol events, that occurred in January, May and June 2002, are listed in

Table 10.11. Twenty-four hour average concentrations of SO_2 , NO , NO_2 , NO_x , CO , $\text{PM}_{2.5}$, PM_{10} (measured by high volume sampler) and PMF mass is included, together with the aged aerosol contributions. The range of $\text{PM}_{2.5}$ concentrations were variable as was the proportion of $\text{PM}_{2.5}$ to PM_{10} (14 to 100%). High aged aerosol contributions were evident in both summer and winter, with three of the events occurring in January.

Table 10.11 Five peak aged aerosol events, 24-hour average data, Christchurch, 2001/2002.

Date	SO_2 ($\mu\text{g m}^{-3}$)	NO ($\mu\text{g m}^{-3}$)	NO_2 ($\mu\text{g m}^{-3}$)	NO_x (ppb)	CO (mg m^{-3})	$\text{PM}_{2.5}$ ($\mu\text{g m}^{-3}$)	PM_{10} Hivol ($\mu\text{g m}^{-3}$)	Aged aerosol ($\mu\text{g m}^{-3}$)	PMF mass ($\mu\text{g m}^{-3}$)
30/1/02	0	3	10	7	0.1	3	21*	4.2	8
16/1/02	6	-	-	7	0.3	11	7	3.8	8
26/6/02	17	-	-	-	3	51	56	3.8	55
22/5/02	20	-	-	-	6	96	111	3.5	97
17/1/02	4	-	-	8	0.3	2	7	3.3	7

*This value was converted from a TEOM at 40°C to a high volume sampler equivalent.

Estimated source contributions and key elemental constituents

The peak aged aerosol event occurred on 30 January 2002. Figure 10.26a and b presents the estimated source contributions, and the main elemental species present in $\text{PM}_{2.5}$, for that day. The $\text{PM}_{2.5}$ concentration on 30 January 2002 was very low ($3 \mu\text{g m}^{-3}$) with an overestimated PMF mass of $8 \mu\text{g m}^{-3}$. On this particular day, the receptor modelling predicted that 51% of the PMF mass was of aged aerosol origin and 48% was secondary particulate. The remaining $\text{PM}_{2.5}$ was attributed to marine aerosol. The main elemental species measured on that day were TC_{mass} (26%), sulphur (24%), nitrate (14%), ammonium (13%) and sodium (13%).

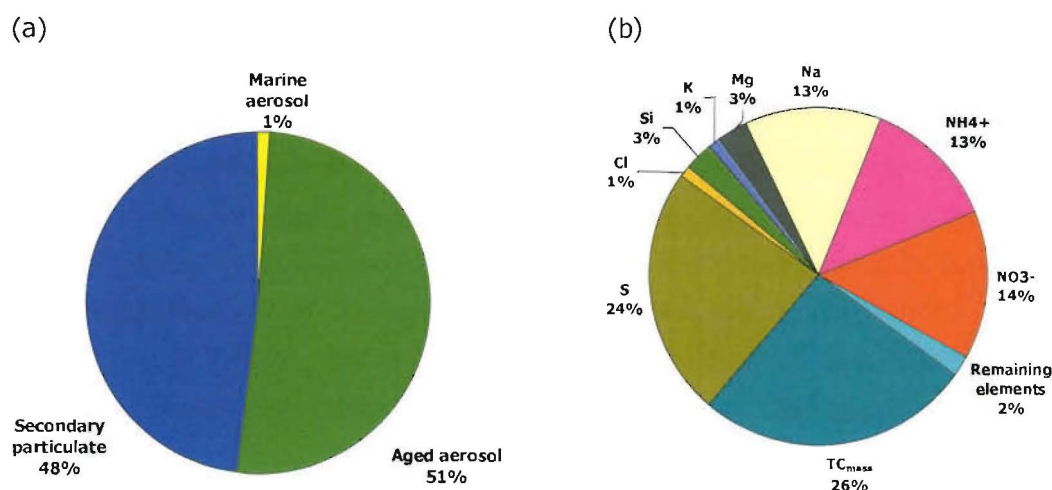


Figure 10.26 Contributions to (a) PMF mass and (b) to the sum of the $\text{PM}_{2.5}$ constituents on 30 January 2002, Christchurch.

Particle characteristics

Figure 10.27 shows a selection of SEM micrographs of particles found on the filter of 30 January 2002 (Note the resolution of the micrographs varies from x11,000 to x19,000). Other than a few large particles, the particulate loading on that day was very low. Nevertheless, there were a variety of particles evident. Figure 10.27a shows a reasonably large particle that appears to be of crustal origin. An EDS scan indicates that the particle is comprised of aluminium, silicon and oxygen suggesting that it may be some type of aluminosilicate soil particle. The particles shown in Figure 10.27b comprise crystals or crustal-type aggregates coated in chain-like combustion particles. The particle in Figure 10.27c, although different in shape to that in (a), also appears to be of soil origin. However, the particle in Figure 10.27d differs from the others. One suggestion is that it is a pollen particle of some variety (Perry Davy, Greater Wellington, *pers. comm.*). The small crystal located towards the top, interestingly, includes potassium, sodium and sulphur but does not include chlorine, and may constitute an aged aerosol compound. In general, the SEM images indicate that the aged aerosol source may comprise a particle mixture including soil, salts containing both sodium and sulphur – but no chlorine – and pollen. These are consistent with the view that this is an aged long-range transport source.

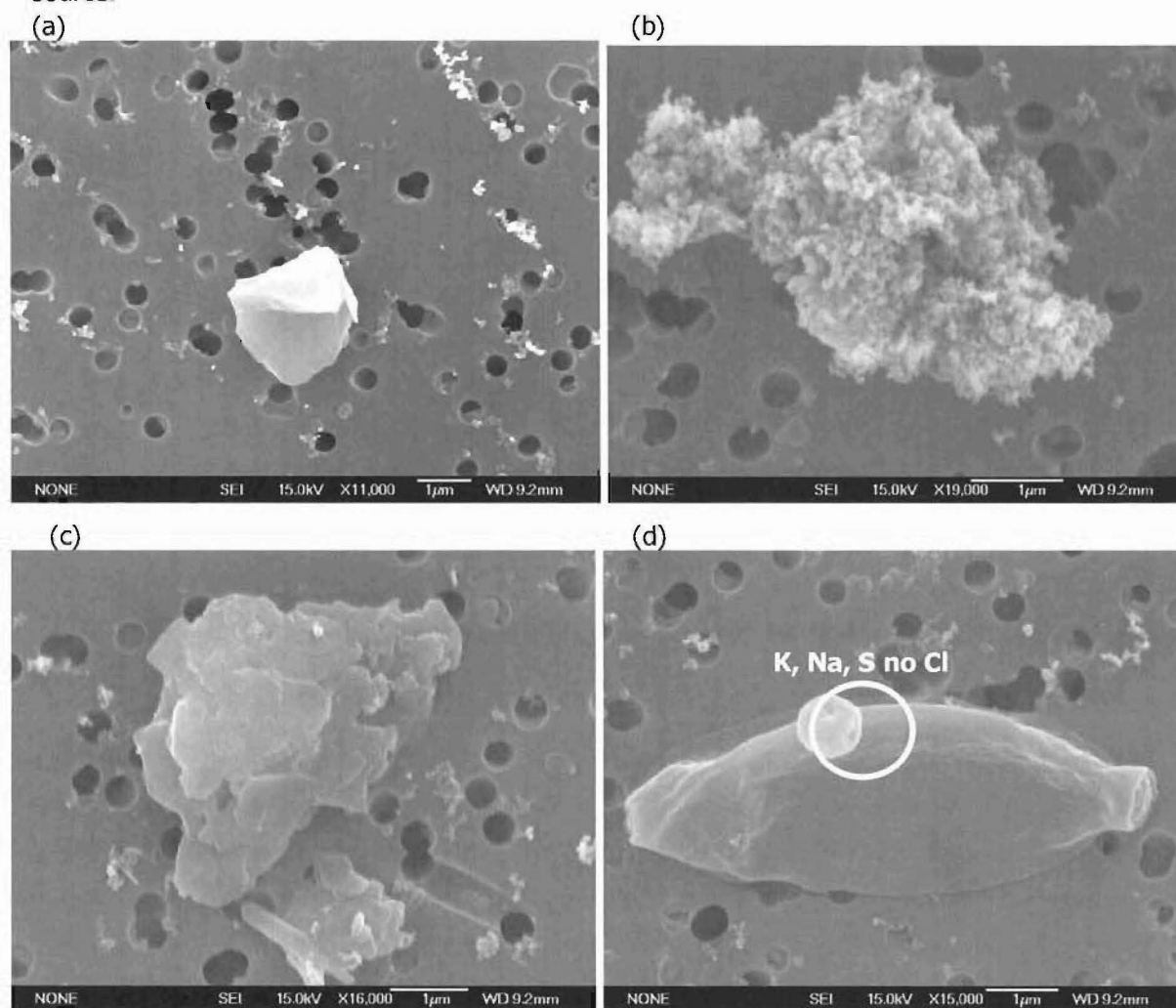


Figure 10.27 Particles sampled onto a polycarbonate filter on 30 January 2002 (NB: the elemental species indicated were identified by the elemental mapping software used).

Temporal variations in meteorology and contaminant concentrations

Figure 10.28a to c shows hourly average contaminant concentrations (including PM₁₀ measured by TEOM, NO, NO₂, NO_x, SO₂ and CO), wind speed and direction, ambient temperature and relative humidity measured at Coles Place, St Albans on 30 January 2002.

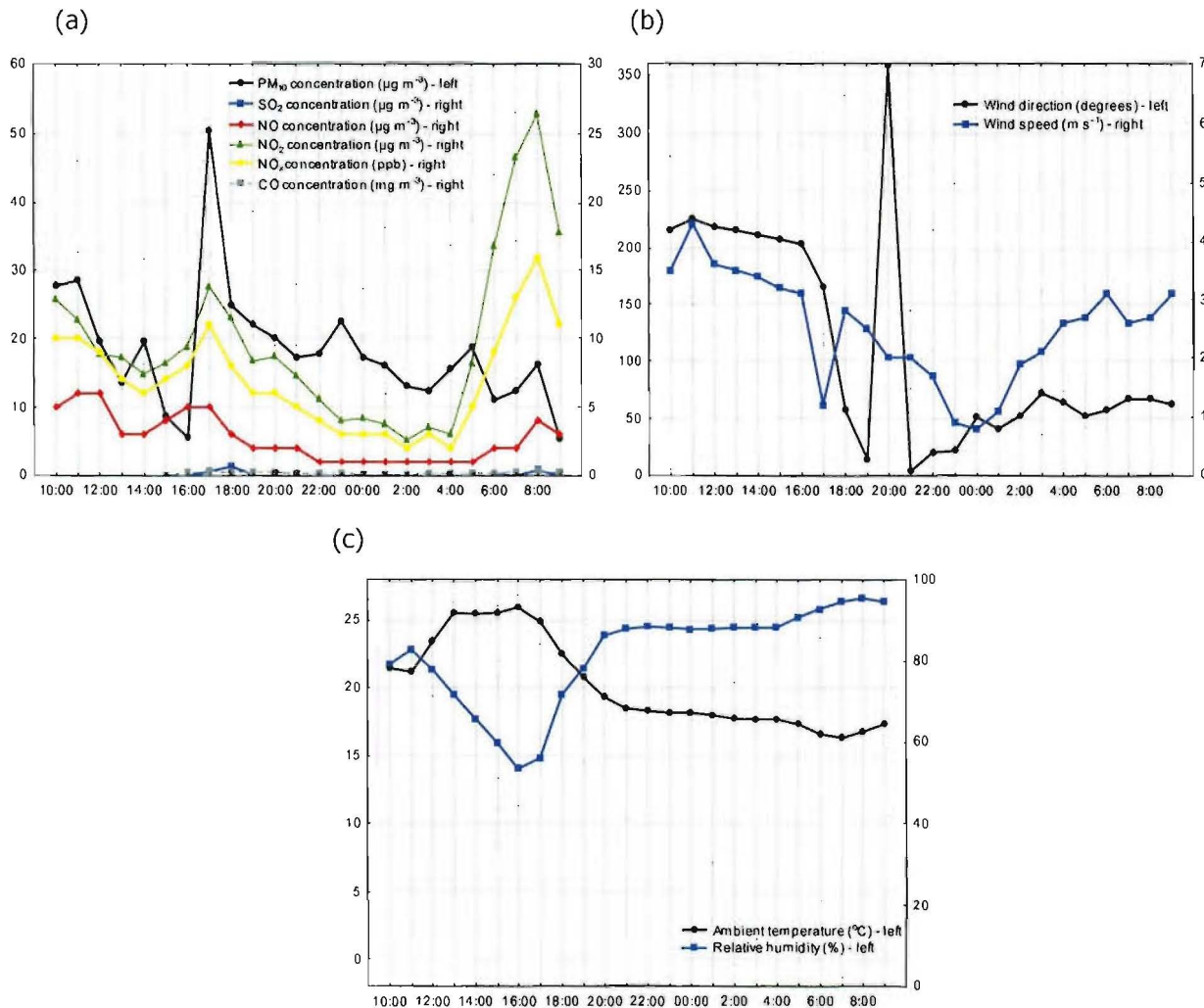


Figure 10.28 Contaminant and meteorological data for 30 January 2002, St Albans, Christchurch.⁶¹

At 10 am on 30 January 2002, concentrations of all contaminants were low, temperatures were around 22°C and moderate winds (3.5 m s^{-1}) were from a southwesterly direction. Contaminant concentrations remained low with a short-duration PM₁₀ peak at 5 pm, coinciding with a calm period. The southwesterly winds persisted for most of the day and then gradually changed to an easterly overnight. Temperatures were warm all day with a mid-afternoon peak of 26°C and a minimum of 16°C around 7 am. Relative humidity was also reasonably high with a low of 55% at 4 pm.

⁶¹ Temperature difference data were unavailable on that day.

Appendix 3 presents a matrix plot of sources and various meteorological variables including wind speed, temperature and relative humidity. The scatter plots for aged aerosol suggest that contributions from this source were higher at lower wind speeds, a variety of temperatures and generally at mid-to-high relative humidity. The correlation analysis presented in Appendix 4 indicates that weak associations with other sources and meteorological variables occur in both summer and winter. In summer, associations with secondary particulate (0.44), motor vehicles (-0.52) and relative humidity (0.3) were found. Secondary particulate and aged aerosol are likely to occur under similar atmospheric conditions as they both include photochemical species. The negative association with motor vehicles is more difficult to explain, but it may be associated with relative humidity. Motor vehicle contributions tend to occur under dry atmospheric conditions whereas the aged aerosol is greater at higher humidity. However, in winter, a similar negative association is found with motor vehicles (-0.52) and there is no association with relative humidity (-0.06). The nature of the link between these two sources is therefore uncertain. However, as sulphur was not found in the motor vehicle profile it could be that sulphur derived from diesel vehicles becomes associated with aged aerosol under warm atmospheric conditions.

Aged aerosol is also associated with wind speed in winter, with the highest concentrations occurring under light winds. The meteorological variables most likely to indicate the locational origin of this source are wind speed and direction. Diurnal profiles for these parameters for the remaining four events indicated in Table 10.11 are presented in Appendix 9. All events were characterised by the presence of stronger daytime easterly winds (up to 4.5 m s^{-1}) and a change to lighter west or southwesterly winds (northwesterlies were also indicated on one occasion). Relative humidity was moderate with daytime lows of 45 to 60%, and daytime temperatures peaked between 21 and 26°C (the exception was 26 June 2002).

The meteorological information indicates that on each of these days land/sea breeze effects occur with onshore winds predominating throughout the day, and light westerly breezes at night. This suggests that marine aerosol of local origin was transported westwards in the sea breeze. Ambient temperatures were warm and there was sufficient reaction time for NaCl to react with locally-produced SO_x to form Na_2SO_4 , and for the chlorine component of the aerosol to be depleted. This aged aerosol was then transported back across Christchurch, together with pollen and soil particles, in the westerly winds overnight. While the meteorological data suggest this may be occurring, further work and monitoring would be required to verify this hypothesis, and to clarify the exact nature of the negative correlation with the motor vehicle source.

10.6 Summary

The PMF receptor model groups elemental species into source profiles and determines source strength on a daily basis. Identification of the sources is the responsibility of the modeller. This chapter evaluated the sources identified by this study by reviewing the chemical composition of each

source, particle morphological characteristics, and temporal patterns in various contaminant concentrations and meteorology. This enabled the model results to be evaluated against the physical evidence and the environmental context.

All of the profiles identified in this study were similar to those found elsewhere. Seasonal patterns in source contributions generally followed those expected, with the greatest wood combustion and motor vehicle contributions in winter, and marine aerosol in summer. Aged aerosol did not exhibit seasonality and secondary particulate was greatest in winter, rather than summer (as demonstrated in other studies). SEM micrographs of particles present on selected filters appeared to be consistent with the sources identified, where sticky organics and inorganic potassium salts were present on the wood combustion filter, NaCl salts on the marine aerosol filter, small crystals that may constitute NH_4NO_3 salts on the secondary particulate filter and a combination of non-chloride salts, particles of crustal origin and pollens on the aged aerosol filter.⁶² Wood combustion contributions were greatest when wind speeds were low and a strong temperature inversion was evident, motor vehicles under low temperature and wind speed conditions, and when an inversion coincided with peak hour traffic, marine aerosol when winds were elevated and with an easterly aspect (but not always), secondary particulate when wind speeds were low, temperatures were relatively warm and relative humidity was moderate, and aged aerosol under warm conditions when easterlies blew during the day and westerlies during the night. This evidence suggests that, overall, the source identification makes physical sense and provides a reasonable representation of the main sources contributing to $\text{PM}_{2.5}$ at Coles Place. However, it is important to note that the wood combustion source was not limited to residential heating (also included outdoor burning and industrial wood combustion), and a combination of sources were responsible for the secondary particulate and aged aerosol contributions.

⁶² Micrographs were not available for the motor vehicle filter.

Chapter 11: Evaluation of model output and comparison with emission inventory estimates

It is important to evaluate the ability of the model to quantify contributions to $PM_{2.5}$, as well as the appropriateness of the factor identification. An assessment of this nature is presented in the following chapter. The extent to which the model explained the measured elemental concentrations was determined by reviewing the model residuals and the proportion of $PM_{2.5}$ accounted for by the elemental measurements. This assessment is important as it determines the applicability of the study results. If, for example, the measured chemical species only account for a small proportion of the mass, then the receptor model results can only explain a small amount of the $PM_{2.5}$. The sources identified and their relative contributions to concentrations were also evaluated against box-modelled emission inventory data to determine whether similar results were obtained.

11.1 Examination of the residuals

Multiple runs of the PMF receptor model were required to determine the correct number of factors, and to optimise the model parameters and final results. The weighted residual matrix, output by the model after each run, was used to determine the adequacy of the model in explaining observed concentrations. The residuals were indicative of model fit, providing information about the amount of elemental mass that could not be explained by the five resolved factors. Consecutive runs were conducted until acceptable residuals were achieved and the factors made physical sense. The frequency distributions of the weighted residuals (scaled by the standard deviations) obtained for the final five-factor solution, are presented in Figure 11.1. Paatero (2002b) suggests that if the correct number of factors is selected, and if the errors are appropriately allocated, the residuals should be within -2 and 2.

The scaled residuals for all modelled elemental species presented in Figure 11.1, are normally distributed. With the exception of some outlier values, most species were modelled effectively with the majority of the residuals between -2 and 2. These included aluminium, calcium, chlorine, chromium, iron, magnesium, sodium, ammonium, nickel, sulphur and silicon. Broader distributions were evident for potassium, nitrate, TC_{mass} and zinc. Concentrations of these species were most variable, with substantial differences between summer and winter concentrations. Concentrations

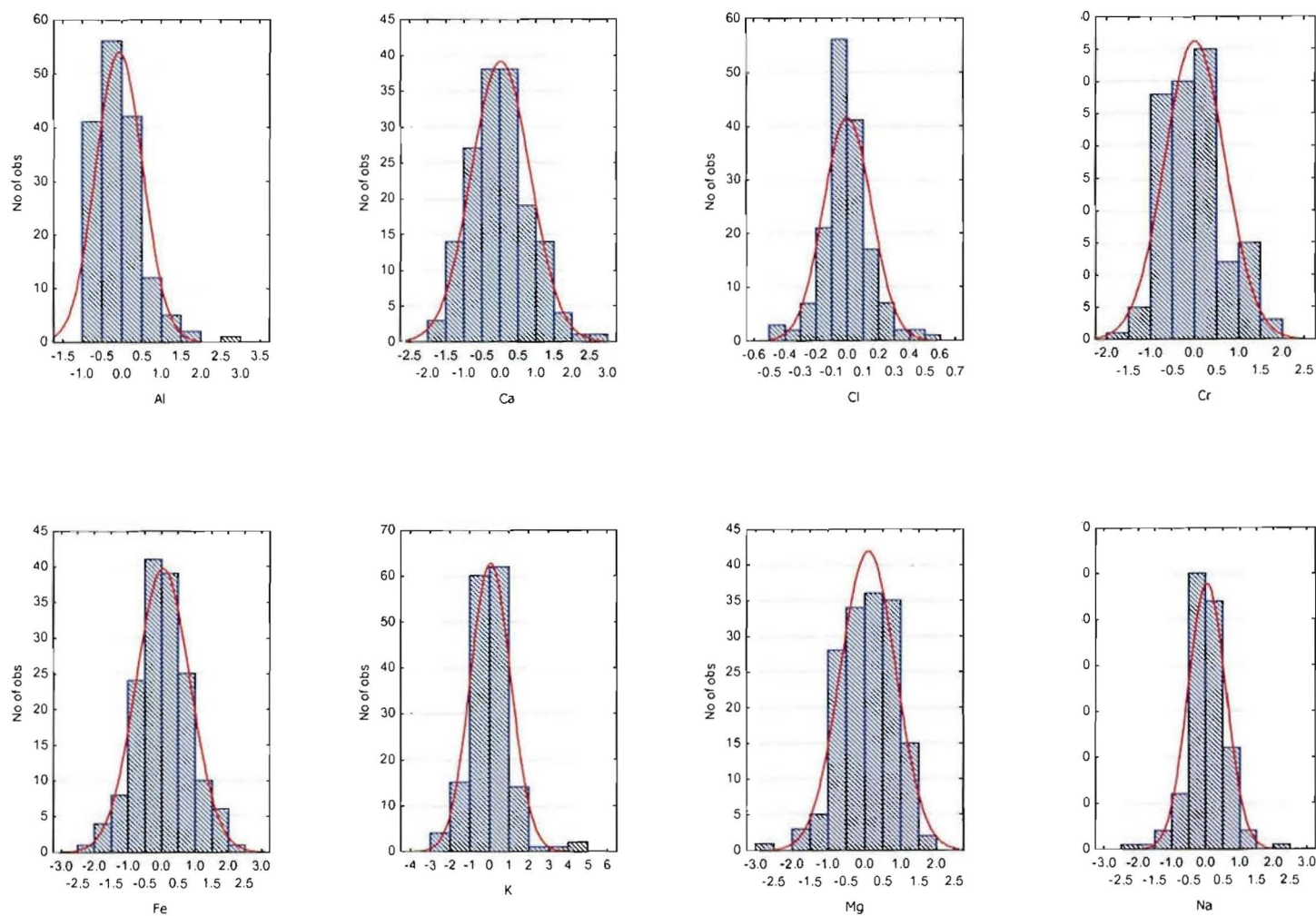


Figure 11.1 Model residuals, five-factor solution, Christchurch, 2001/2002 (arbitrary units)

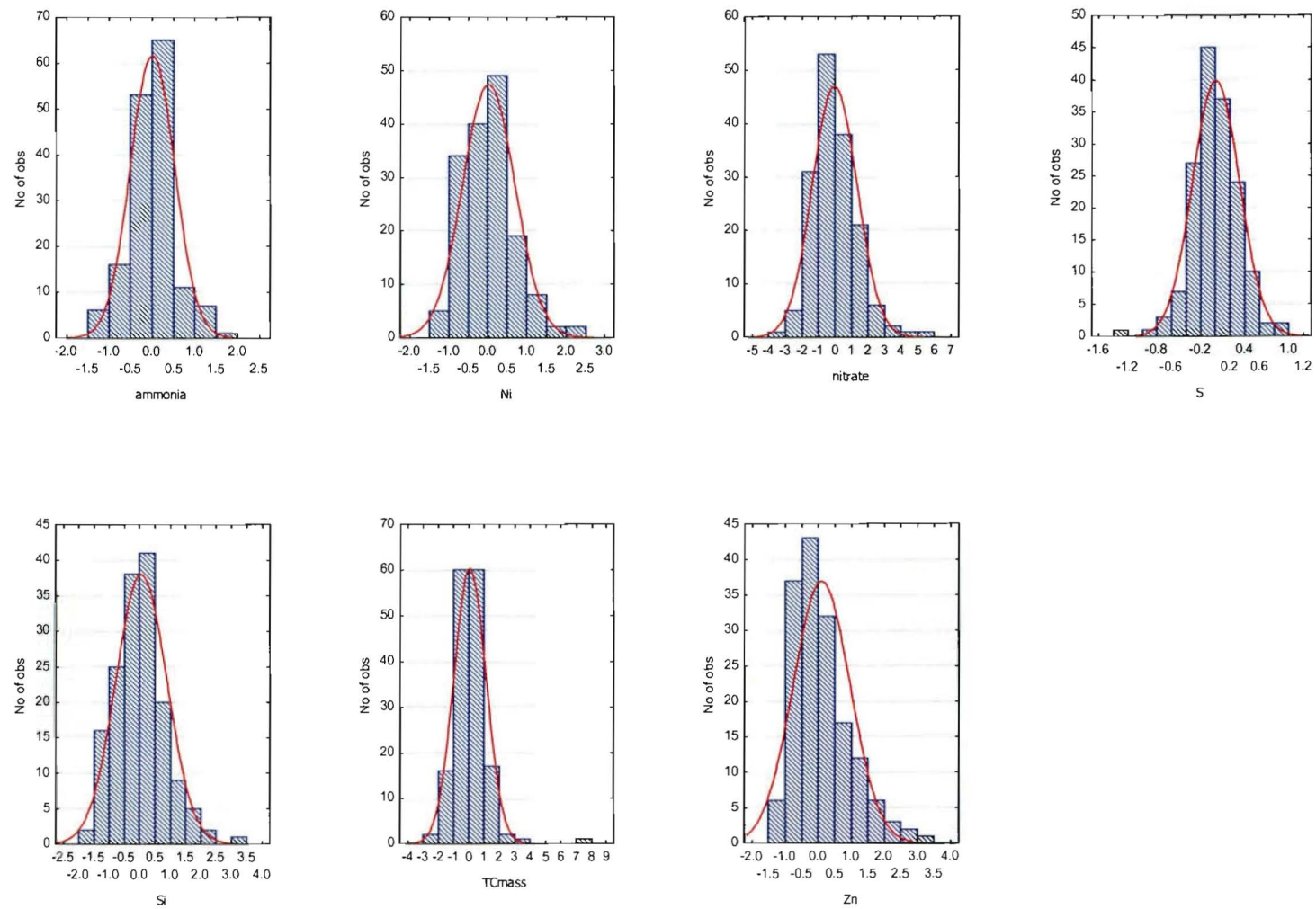


Figure 11.1 continued.

leading to high residuals were individually examined for validity during the modelling, and if anomalous, were down-weighted.⁶³ The distributions illustrated in Figure 11.1 appear to be reasonable, relative to other published PMF studies (e.g. Lee *et al.*, 2002b; Polissar *et al.*, 1998). This indicates that the modelling has accounted for most of the measured concentrations and therefore provides a good representation of PM_{2.5} in Christchurch.

11.2 Mass reconstruction

The ability of the receptor model to accurately represent sources of PM_{2.5}, however, is reliant on the quantity of PM_{2.5} mass actually accounted for by the elemental measurements, as well as the amount of elemental mass explained by the resolved factors. The latter, described in Section 11.1, was evaluated by reviewing the residuals and the former by “reconstructing” PM_{2.5} mass. Two methods were used to determine the quantity of mass accounted for by the measured elemental sum, and the results of the “mass reconstruction” are outlined below.

11.2.1 Conversion method

Accurately quantifying the elemental mass accounted for by the chemical species measured is not a simple task. Mass may be over or underestimated depending on factors such as sample moisture, and the conversion factors used to estimate molecular mass.

PM_{2.5} mass was determined gravimetrically by measuring the filter prior to and following sampling. The filters were conditioned for 24-hours, at a specific humidity, prior to weighing. The quantity of water present in the sample was unknown and dependent on the relative humidity at the time of weighing and on the composition of the particles. A high moisture content can potentially result in greater PM_{2.5} mass measurements that are difficult to reconstruct using the elemental data (when summed), as these are not affected by moisture.

The analytical technique used to measure elemental concentrations, PIXE, only provides measurements for individual elemental species rather than their molecular compound forms. Important species such as hydrogen, oxygen and nitrogen are not measured and conversion factors are required to account for contributions of these species to molecular mass. Mass may be “reconstructed” using a variety of conversion factors, which differ depending on the assumptions and chemical species used (e.g. Solomon *et al.*, 1989; Lewis *et al.*, 2003; Castanho and Artaxo, 2001). The approach adopted by Brook *et al.* (1997) was used to reconstruct mass for this study, as follows:

$$\text{Mass}_{\text{rec}} = \text{SO}_4^{2-} + \text{NO}_3^- + \text{NH}_4^+ + 1.79\text{V} + 1.24\text{Zn} + 1.12\text{Ba} + \text{Pb} + \text{Br} + \text{Cl} + \text{Na} + \text{SOIL} + \text{Rem} \quad [24]$$

$$\text{SOIL} = 2.20\text{Al} + 2.49\text{Si} + 1.63\text{Ca} + 1.58\text{Fe} + 1.94\text{Ti} + 1.41\text{K} \quad [25]$$

$$\text{Rem} = \Sigma(\text{all remaining elements}) \quad [26]$$

⁶³ Down-weighting refers to the process of allocating higher error estimates for a particular concentration. This reduces the importance of this value in the modelling.

To determine the proportion of $\text{PM}_{2.5}$ mass accounted for by the elemental measurements collected during this study, the concentrations were multiplied by the factors indicated in the equations above, then summed and plotted against the gravimetric $\text{PM}_{2.5}$ concentrations.⁶⁴ Carbon was included as TC_{mass} , where the OC_{mass} ($\text{OC} \times 1.4$) values were added to the EC measurements. Figure 11.2 presents reconstructed $\text{PM}_{2.5}$ mass. Assumptions associated with the approach adopted by Brook *et al.* (1997) were:

- All NO_3^- is NH_4NO_3 .
- SOIL accounts for the main crustal elements in their oxidised forms and is scaled up by 14% to account for other soil elements not otherwise included.
- Aluminium is only of soil derivation and is in the form Al_2O_3 .
- Vanadium, barium and zinc are present in their oxidised forms and solely derived from high temperature combustion/industrial processes.
- Lead is of motor vehicle origin and associated with fine bromine and chlorine.
- Sodium is associated with sulphur.
- Soil and smoke-derived potassium is present as K_2O .

It is uncertain how valid these assumptions are for $\text{PM}_{2.5}$ in Christchurch. Nevertheless, this approach allows broad estimates to be derived.

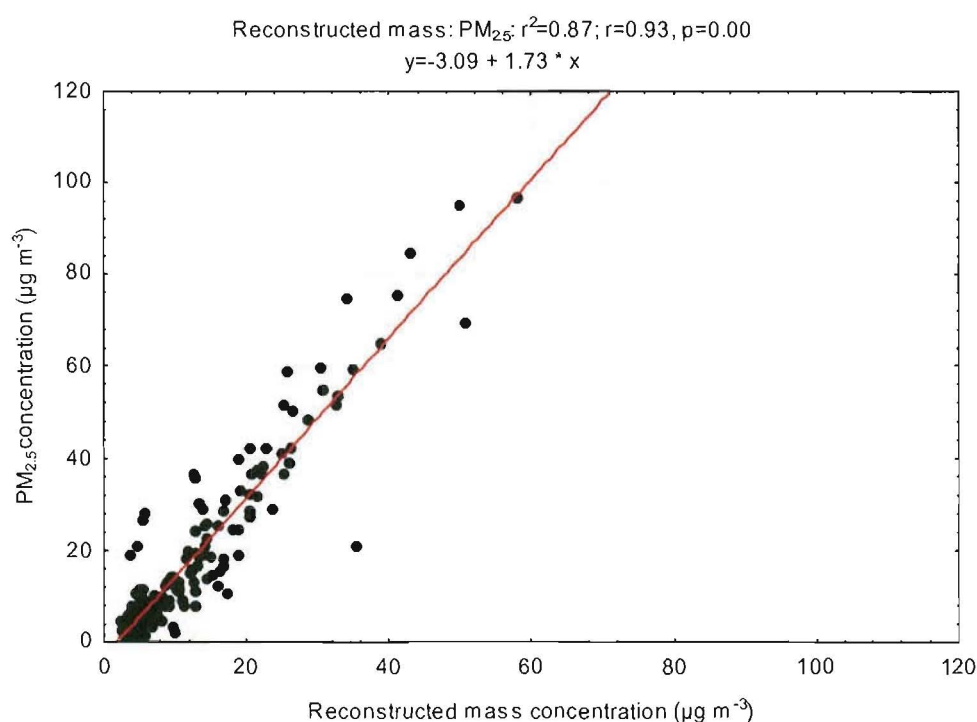


Figure 11.2 Reconstructed $\text{PM}_{2.5}$ mass, 24-hour averages, Christchurch, 2001/2002.

⁶⁴ Species excluded from the receptor modelling were included in the reconstructed mass. With the exception of sulphate, these would not vary reconstructed mass significantly as they were originally excluded because of high frequencies of zero concentration data. The sulphate measurements were used in place of sulphur, as particulate sulphur is mainly present as sulphate. Otherwise, sulphate would have been estimated from sulphur using a conversion factor.

At low concentrations, $PM_{2.5}$ mass was often overestimated by the reconstructed mass. If it was assumed that 100% of mass was accounted for on those days, then approximately 79% of summertime $PM_{2.5}$ and 74% of wintertime $PM_{2.5}$ was explained, on average, by the reconstructed mass. Although most of the $PM_{2.5}$ has been accounted for by the elemental measurements, 21 to 26% remained unexplained. The unexplained component was most likely due to factors such as sample moisture and the potential underestimation of OC_{mass} (1.4 may not be a sufficient conversion factor for wood smoke dominated areas). These issues will be discussed later in the chapter.

11.2.2 Sum of the source contributions

Mass may also be reconstructed by summing the daily source contributions derived from the receptor modelling. The daily contributions were obtained by multiplying each daily factor score (G-Factor values) by the sum of the F-Factor contributions. Figure 11.3a presents reconstructed mass (explained PMF mass) based on the G and F-Factors. The relationship between $PM_{2.5}$ and explained PMF mass is essentially the same as that for the reconstructed elemental sum (Figure 11.2), confirming that the PMF receptor model provides a good representation of the elemental measurements.

It is generally accepted in the literature that while the elemental measurements will not account for 100% of measured $PM_{2.5}$ (thus leading to underestimated PMF mass), a linear combination of the source contributions will be responsible for the entire $PM_{2.5}$ mass (Polissar *et al.*, 2001). Consequently, the factor scores are usually regressed against $PM_{2.5}$ mass using MLR and then multiplied out by the obtained B coefficients (Section 9.3).

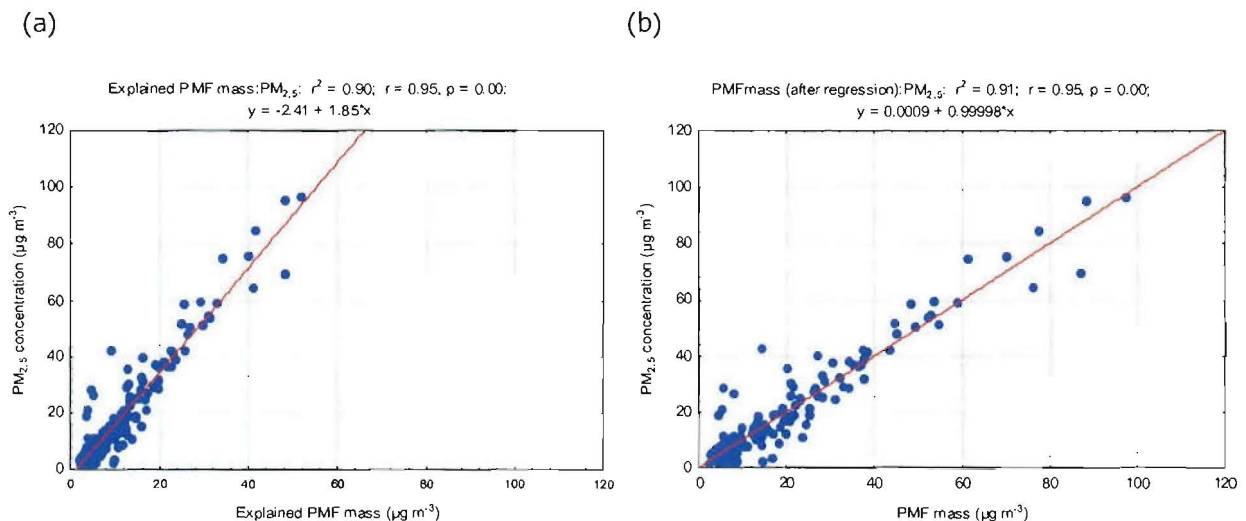


Figure 11.3 Explained PMF mass (a) prior to regression and (b) after regression, 24-hour averages, Christchurch, 2001/2002.

Figure 11.3a shows a good linear relationship between explained PMF mass and $PM_{2.5}$ (r^2 value of 0.90). It was appropriate, therefore, for the source contributions to be scaled up to $PM_{2.5}$. Figure 11.3b presents regressed mass (PMF mass) estimates plotted against the $PM_{2.5}$ measurements. The

PMF mass and $\text{PM}_{2.5}$ concentrations were very similar in this instance. Again, if it is assumed that on days when mass was overestimated, 100% of mass was accounted for, then approximately 87% of summertime $\text{PM}_{2.5}$ and 94% of wintertime $\text{PM}_{2.5}$ was explained, on average, by the PMF mass. On this basis, the PMF receptor model has provided an excellent representation of the main sources contributing to $\text{PM}_{2.5}$ in central Christchurch.

However, the quality of the modelling varied considerably by season as illustrated in Figure 11.4a and b. In summer, $\text{PM}_{2.5}$ mass was underestimated at concentrations exceeding $8 \mu\text{g m}^{-3}$. Conversely, during the winter months, there was relatively less scatter in the data and a strong relationship between PMF mass and $\text{PM}_{2.5}$ ($r^2 = 0.91$) existed. This variation was a consequence of the amount of $\text{PM}_{2.5}$ explained by the elemental measurements, rather than the PMF receptor model's ability to adequately represent summertime $\text{PM}_{2.5}$ (Figure 11.5).

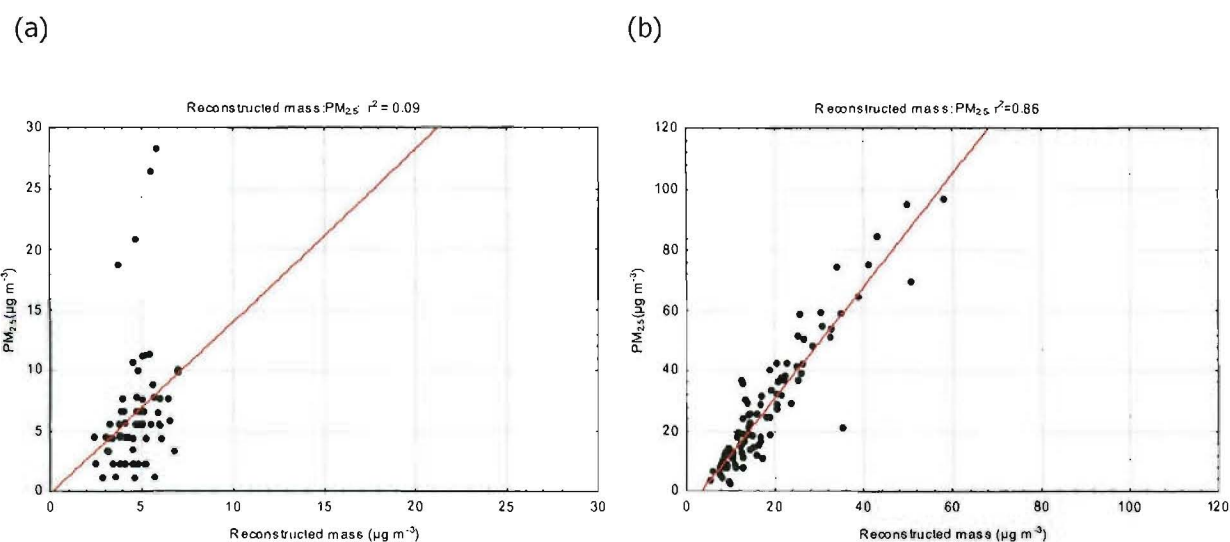
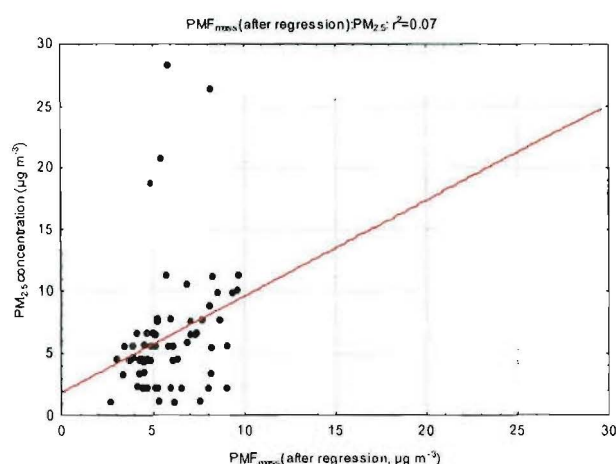


Figure 11.4 Relationship between $\text{PM}_{2.5}$ and PMF mass in (a) summer and (b) winter, 24-hour averages, Christchurch 2001/2002.

Figure 11.5a and b present reconstructed mass (calculated using the equations in Section 11.2.1) and show that peak summertime concentrations were poorly explained by the elemental measurements. It is uncertain why these concentrations were underestimated, but it was most likely due to inadequacies in the carbon measurements. This is discussed further in the following sections. Despite these concerns, PMF mass provided an excellent representation of $\text{PM}_{2.5}$ at the time of year when elevated concentrations were of greatest concern from an air quality management perspective.

(a)



(b)

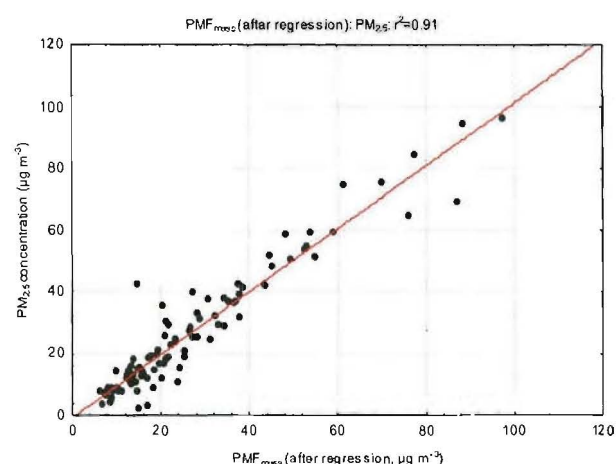


Figure 11.5 Relationship between $\text{PM}_{2.5}$ and reconstructed mass in (a) summer and (b) winter, 24-hour averages, Christchurch 2001/2002.

11.2.3 Unexplained $\text{PM}_{2.5}$ mass

A number of studies have discussed issues associated with unexplained $\text{PM}_{2.5}$ mass (i.e. as calculated using the conversion method in Section 11.2.1). Andrews *et al.* (2000) reviewed information from a wide range of studies and concluded that there was a strong association between unexplained $\text{PM}_{2.5}$ mass and OC concentrations. Possible errors in the sampling and analysis of OC, inaccurate estimates of OC_{mass} from OC measurements, and water adsorption by organics were suggested as possible contributing factors. In addition, it was reported that the proportion of unexplained mass was greatest when particles were of anthropogenic origin or discharged from forest fires.

When mass was reconstructed during this study using the conversion method, approximately 21 to 26% of the $\text{PM}_{2.5}$ could not be explained by measured elemental mass (although only 6 to 13% remained unexplained after the modelling was conducted). To investigate whether there were links between unexplained mass, source type and chemical species, the daily source contributions and chemical concentrations were plotted against unexplained mass. These are presented in the matrix plots in Appendix 10. The most distinct associations appeared to exist between unexplained mass and $\text{PM}_{2.5}$, TC_{mass} , potassium, BC and wood combustion. As $\text{PM}_{2.5}$ concentrations increased, it was progressively more difficult to account for $\text{PM}_{2.5}$ mass by the elemental measurements. Also, as potassium, BC, TC_{mass} and the wood combustion source concentrations increased, the amount of unexplained mass also increased. While further investigation would be necessary to confirm the exact cause(s) of the unexplained mass, the correlations indicate a possible link with the wood combustion source. OC, a key component of wood smoke, is often associated with unexplained mass (Andrews *et al.*, 2000) and it is quite feasible that this was a factor in Christchurch. Measurement issues associated with OC (e.g. varying particle moisture) and/or the use of an insufficient conversion factor (to calculate organic molecular mass) may at least partially account for the underestimates

observed. OC could also be responsible for the underestimation of summertime mass, as Andrews *et al.* (2000) found that the relationship between unexplained mass and OC persisted even at low concentrations.

11.3 Comparison with box-modelled emission inventory results

To evaluate the ability of the PMF receptor model to resolve the main sources and quantify the relative contributions to PM_{2.5} in Christchurch (in the form of PMF mass), the data were compared with emission inventory derived estimates. The 2002 Christchurch emission inventory (Scott and Gunatilaka, 2004) provided a detailed assessment of the key sources of anthropogenic emissions of various contaminants, including PM_{2.5} for an average 2002 winter's day. Receptor-modelled results obtained for the wintertime period were compared to these estimates. However, as the inventory only allowed relative source contributions to emissions rather than concentrations to be calculated, further work was needed to convert the emission inventory data into predicted concentrations. This was conducted using a chemical box model (Section 3.4). This chapter outlines the box model method used, how it was adapted for the assessment and compares the final results with those from the receptor modelling.

11.3.1 The 2002 Christchurch emission inventory

Several emission inventories have been prepared for the Christchurch area. These include the 1996, 1999 and 2002 Inventories (NIWA, 1998; Wilton, 2001a; Scott and Gunatilaka, 2004). Each inventory quantified anthropogenic emissions of various contaminants, for a typical winter's day (24-hour period). The key source sectors were identified as residential heating, industry and commerce, and motor vehicles. The 2002 estimates were selected for comparison as PM_{2.5} emissions were included in the 2002 inventory, and it was conducted at the same time as this study.

Emission inventories, as outlined in Section 4.1, estimate emissions by collecting source activity and fuel use information, and multiplying these values by an emission factor. Emission factors are representative values that provide a measure of contaminant discharge for a specific type of activity and fuel consumption. These are developed (ideally) from a set of direct source emission tests and represent the long-term average of all sources within a set category. The activity data in Christchurch were collected using a variety of methods. A representative sample of households (e.g. 714 surveys provided sufficient data to represent the 55,695 households present in Inner Christchurch, with an error estimate of 3.5%) was surveyed and provided information on the type of residential heating used to heat the main living area, age of appliances, and type and quantity of heating fuel used (Lamb, 2003). The emission factors were based on local and overseas "real-life" emissions data. Motor vehicle activity data, in the form of vehicle kilometres travelled (VKT), were provided by a "vehicle driver" trip/travel demand model. The model represented trips made by motorised vehicles in Christchurch within defined timeframes. VKT were estimated for different time

periods, driving conditions (including free-flow, interrupted and congested), and urban categories (e.g. central urban and suburban). Fleet-weighted, corridor flow emission rates were used to determine emissions from the VKT estimates. The emission rates/factors were derived from in-use vehicle emission tests conducted by the MoT (MoT, 1998). The amount of industrial and commercial activity was determined by distributing questionnaires to all industries consented by Environment Canterbury. Information collected included type of activity, quantity of material used, process rates, fuel type and consumption, and the nature of control equipment used. Where survey data were unavailable, consent information, or previous emission inventory data were used. The emission factors applied were mostly derived from the USEPA's AP-42 database, and supplemented with local data, where possible. Emissions calculated from each source were aggregated into source sector totals for five different time periods – 6 am to 10 am, 10 am to 4 pm, 4 pm to 10 pm, 10 pm to 6 am, and 6 am to 6 am.

The major sources and their relative contributions to anthropogenic emissions of $PM_{2.5}$, as determined by the 2002 inventory, are summarised in Table 11.1. Emissions from the Inner Christchurch area were likely to be most representative of those experienced in the vicinity of the receptor site at Coles Place and the assessment was conducted using these data.

Table 11.1 Source contributions to anthropogenic $PM_{2.5}$ for a 24-hour wintertime period in Christchurch, 2002 (Scott and Gunatilaka, 2004 and adjusted following Scott, 2005a).

Inner Christchurch	2002 inventory $PM_{2.5}$ (t)	Total (%)	Revised 2002 $PM_{2.5}$ (t)	Total revised $PM_{2.5}$ (%)
Residential heating	4.70	88%	3.23	83%
Industry/commerce	0.11	2%	0.11	3%
Motor vehicles	0.54	10%	0.54	14%
Suburban Christchurch	2002 inventory $PM_{2.5}$ (t)	Total (%)	Revised 2002 $PM_{2.5}$ (t)	Total revised $PM_{2.5}$ (%)
Residential heating	8.92	86%	6.13	81%
Industry/commerce	0.49	5%	0.49	6%
Motor vehicles	0.94	9%	0.94	13%
Outer Christchurch	2002 inventory $PM_{2.5}$ (t)	Total (%)		
Residential heating	1.43	77%		
Industry/commerce	0.21	11%		
Motor vehicles	0.22	12%		
Metropolitan Christchurch	2002 inventory $PM_{2.5}$ (t)	Total (%)		
Residential heating	10.35	85%		
Industry/commerce	0.70	6%		
Motor vehicles	1.16	10%		

However, in 2005 the 2002 emission inventory data were revised by Environment Canterbury (Scott, 2005a) on the basis of more recent fuel-use information. The 2002 estimates were too high and

were subsequently adjusted and new emission estimates calculated. The relative contribution of anthropogenic emissions to PM_{2.5} on an average winter's day in Inner Christchurch was revised from 88% to 83% for residential heating, from 2% to 3% for industry and commerce, and from 10% to 14% for motor vehicles (Table 11.1).

11.3.2 Chemical box model

There are a number of models that may be used to simulate atmospheric processes and predict contaminant concentrations. These include box models and three-dimensional atmospheric chemical transport models. Three-dimensional models are extremely complex and require detailed atmospheric and spatial contaminant data, which are not easy to obtain. Box models, conversely, are relatively simple to use and require less input data. As a model had been developed for the Inner Christchurch area by Gimson and Fisher (1997), this was used for the evaluation of the receptor-modelled estimates against emissions inventory data.

Essentially, a box model represents an entire atmospheric area of interest (usually an airshed) as a simple, single box. The concentrations and meteorological variables within the box are assumed to be relatively uniform and only vary by time (Seinfeld and Pandis, 1998). Concentrations predicted by the model are determined by the sources contributing to emissions, surface deposition, emission sinks and inflow and outflow of PM_{2.5} from the defined space (Gimson and Fisher, 1997).

The model developed by Gimson and Fisher (1997) represented the Inner Christchurch area including the Christchurch CBD, Beckenham/Sydenham, Fendalton, Linwood, Opawa, Riccarton, Shirley, Spreydon and St Albans. The box dimensions were determined by the physical extent of the Inner Christchurch area (length scale = 8.75 km) and the height of the mixing layer (which varied over time). The model was set-up to simulate the influence of meteorological variables such as wind speed, air temperature and height of the mixing layer on emissions under conditions conducive to high pollution. Meteorological data for maximum PM₁₀ days were used as input for the model and were typified by low wind speeds and the presence of strong temperature inversions.⁶⁵ Emissions representing an "average winter's day" were transformed by the model into maximum concentrations. The 24-hourly average concentrations were determined as follows (Gimson and Fisher, 1997):

$$C_o = 0 \quad [27]$$

$$C_{j+1} = \frac{100}{h_j} E_j + (1 - 0.41u_j) C_j \quad [28]$$

The 24 hour average is then calculated by:

⁶⁵ The conditions that lead to high PM₁₀ are likely to be the same as those that produce high PM_{2.5} concentrations. It has been reported that on days when PM₁₀ is elevated, most particles are present in the fine particle fraction (Foster, 1998a).

$$C = \frac{1}{24} \sum_{j=1}^{24} C_j \quad [29]$$

Table 11.2 **Formulae definitions and units**

Equation term	Definition	Units
C	24-hour mean PM ₁₀ concentration	µg m ⁻³
C_j	PM ₁₀ concentration at hour j	µg m ⁻³
$j=0$ $j=1$ $j=24$	1400 hours day 1 1500 hours 1400 hours day 2	
h_j	Mixing height, between hours j and $j+1$	m
E_j	Total emission from all sources between hours j and $j+1$	g ha ⁻¹
u_j	Hourly wind speed	m s ⁻¹

Gimson and Fisher (1997) evaluated the ability of the model to predict 24-hour concentrations for a total of 17 high pollution days. The meteorological conditions for the 12 and 13 June 1991 simulation were used to transform the revised 2002 inventory emissions into predicted concentrations. This particular day was selected as an excellent ratio of 0.99 for modelled versus observed concentrations had been achieved (Gimson, 1998). The predicted 24-hour PM₁₀ concentration for 12 and 13 June 1991 was 170 µg m⁻³. This estimate was lower than maximum PM₁₀ concentration in 2002 (252 µg m⁻³) but was higher than maximum PM₁₀ measured on the sampling days of this study. In this regard, the meteorological conditions for the 12 and 13 June 1991 were viewed as adequate for modelling 2002 emissions data.

The input data used by Gimson (1998) for 12 and 13 June 1991 simulation and for this assessment comprised:

1. A combination of simulated data and arbitrary estimates representative of mixing heights. These were evaluated against actual observations (Gimson, 1998).
2. Dry deposition velocity based on aerodynamic theory and actual observations.
3. Meteorological data such as wind speeds derived from actual measurements.

The emission estimates used were the revised PM_{2.5} emissions for 2002, as provided by Environment Canterbury. These were only available for a 24-hour period. However, the box model required hourly data, so the revised 2002 24-hour PM_{2.5} total was converted into hourly emissions using the proportional distribution of emissions from the 1991 simulation. The estimated hourly emissions data, together with the 1991 input data used are presented in Table 11.3. As indicated previously, with the exception of emissions, the model inputs are identical to those used in the 1991 simulation (Gimson, 1998).

The model predicted a maximum 24-hour average $\text{PM}_{2.5}$ concentration of $97 \mu\text{g m}^{-3}$ from the redistributed and revised 2002 emissions data. This was similar to the maximum $\text{PM}_{2.5}$ concentration ($96.3 \mu\text{g m}^{-3}$) measured during this study, suggesting that the box model would provide a reasonable representation of peak 2002 $\text{PM}_{2.5}$ concentrations. The model results therefore could be used to determine the relative contributions of the different sources to concentrations.

The relative contribution of each source sector to concentrations was determined by evaluating the impact of emissions from each individual sector on the predicted 24-hour average $\text{PM}_{2.5}$ concentration. That is, input emissions data for two of the sources (e.g. motor vehicles and residential heating) were adjusted to zero and a concentration predicted from the remaining emissions (i.e. industry and commerce). This was repeated for the other two sources and the proportion of the individual sector concentrations to the combined concentration ($97 \mu\text{g m}^{-3}$) provided the relative contributions to 24-hour average $\text{PM}_{2.5}$.

Table 11.3 Hourly box model input data for Inner Christchurch, 2002 (revised 2002 emissions data provided by Environment Canterbury; Gimson, 1998).

Time	Wind speed (m s^{-1})	Wind direction (degrees)	Mixing height (m)	Residential heating emissions (kg hr^{-1})	Industry and commerce emissions (kg hr^{-1})	Motor vehicle emissions (kg hr^{-1})
09:00	0.7	308	500	13.2	2.4	8.1
10:00	1.6	243	500	20.6	0.8	8.8
11:00	1.2	246	500	10.3	0.8	4.4
12:00	1.2	239	500	10.3	0.8	4.4
13:00	1.4	245	500	10.3	0.8	4.4
14:00	1.2	254	500	10.3	0.8	4.4
15:00	1	315	500	20.6	0.8	8.8
16:00	1.3	329	500	35.1	0.9	6.3
17:00	0.8	307	100	70.2	0.9	6.3
18:00	0.9	231	100	70.2	0.9	6.3
19:00	0.6	172	100	70.2	0.2	3.1
20:00	0.6	321	70	70.2	0.2	3.1
21:00	0.5	206	70	35.1	0.2	3.1
22:00	0.6	249	25	9.9	0.7	0.1
23:00	0.4	214	25	9.9	0.7	0.1
00:00	0.7	255	25	9.9	0.7	0.1
01:00	0.8	247	25	6.0	0.7	0.1
02:00	1.5	228	25	6.0	0.7	0.1
03:00	1.3	251	25	6.0	0.7	0.1
04:00	0.9	164	25	6.0	0.7	0.1
05:00	0.7	312	25	6.0	0.7	3.4
06:00	0.9	32	25	4.4	0.8	2.7
07:00	1.0	249	150	13.2	0.8	2.7
08:00	0.8	209	300	13.2	0.8	8.1

The relative source contributions to PMF mass, determined using the PMF receptor model, were available for 159 days extending throughout the summer and winter months. Table 11.4 presents

relative contributions to peak $PM_{2.5}$ concentrations based on the box-modelled revised emission inventory estimates; and peak PMF mass, average PMF mass on days when PM_{10} exceeded $50 \mu g m^{-3}$ (i.e. current NES threshold value) and the average contributions over the entire winter period, as determined by the PMF receptor model. As the box model predicted a 24-hour average $PM_{2.5}$ concentration of $97 \mu g m^{-3}$, and the peak receptor-modelled concentration was also $97 \mu g m^{-3}$, it may reasonably be assumed that the most appropriate comparison between methods was with the peak $PM_{2.5}$ day (22 May 2002).

Table 11.4 Source contributions to predicted wintertime $PM_{2.5}$ and PMF mass in Christchurch, 2001/2002.

Source	Box-modelled emission inventory estimates	Receptor-modelled maximum wintertime contributions	Receptor-modelled average contributions on high PM_{10} days	Receptor-modelled average wintertime contributions
Wood combustion		92%	87%	79%
Residential heating	89%			
Motor vehicles	8%	1%	2%	4%
Industry	3%			
Marine aerosol		2%	2%	3%
Aged aerosol		3%	3%	5%
Secondary particulate		2%	6%	9%

The first feature to note, when comparing the box-modelled emission inventory data with the receptor modelling results, is that the emission inventory quantified contributions from residential heating specifically, and included industrial and commercial contributions. On the other hand, the receptor model resolved a broader wood combustion factor, which included other sources of wood smoke such as wood-fired boilers and outdoor burning. In addition, the receptor model did not resolve an industrial source and included natural and secondary sources such as marine aerosol, secondary particulate and aged aerosol. Although the wood combustion factor could include other sources of wood smoke, on the peak $PM_{2.5}$ day (22 May 2002) contributions from outdoor burning were unlikely to be significant as this activity is banned in Christchurch from May to August. Also, there were only 9 consented wood-fired boilers operating in Inner Christchurch during the winter months of 2002, contributing 1 kg of $PM_{2.5}$ to the winter's day total (Scott and Gunatilaka, 2004). As there were a large number of wood burning residential heaters (23,417) used in Inner Christchurch, contributing 4,122 kg to the total winter's day $PM_{2.5}$, most of the wood combustion contribution on this day would be from residential heating.

Despite these differences, the similarity of the residential heating and wood combustion contributions between source attribution methods is striking (i.e. 92% for wood combustion and 89% for residential heating). Even when the box-modelled data are compared to the average contributions on high pollution days or the average wintertime contributions, wood combustion remained the primary source, contributing 79 to 87% of wintertime $PM_{2.5}$ (Table 11.4). The receptor-modelled motor

vehicle contributions (1%) were not as comparable with the box-modelled estimates (8%) as that of wood combustion. However, the emission inventory estimates only account for primary anthropogenic emissions and therefore the total $PM_{2.5}$ accounted for by the inventory will differ from that of the receptor model. Secondary particles formed from the condensation of gases, and natural sources, were not quantified by the inventory. If the marine aerosol, secondary particulate and aged aerosol components were eliminated from the receptor-modelled totals, wood combustion would contribute 99% of $PM_{2.5}$ on 22 May 2002, with 1% from motor vehicles. This suggests that on maximum pollution days, wood combustion contributions are so dominant, they mask contributions from other sources.

On the surface, it appears that the receptor model may be overestimating the contribution of wood combustion, relative to the emission inventory. However, the box model, which only includes primary emissions,⁶⁶ and the receptor model, which includes natural and secondary components, actually predict the same 24-hour average concentration for the peak $PM_{2.5}$ day ($97 \mu g m^{-3}$). This would then suggest that the inventory and/or the box model is actually overestimating the $PM_{2.5}$ concentration (i.e. the box-modelled $PM_{2.5}$ estimate based on primary emissions only should be lower than both the measured concentrations and receptor-modelled PMF mass which includes PM derived from marine and secondary sources). The overestimate may be occurring in one, two or three of the source sectors and it may be related to the emission data and/or to the assumptions built into the box model. Issues associated with the inventory emissions estimates include the reliability of the emission factors and the fuel use/activity data,⁶⁷ the exclusion of some sources contributing to $PM_{2.5}$ (i.e. non-consented permitted activities), and the fact that the inventory may not account for specific emissions impacting on the receptor site, as it treats emissions in Inner Christchurch in an aggregated way. Several studies have suggested that inaccurate emission estimates are generally responsible for variations between source and receptor models (Ryan *et al.*, 1988; Watson and Chow, 2000; Watson *et al.*, 2000). Watson *et al.* (2002) compared wintertime source contributions from emission inventories (not modelled) and the CMB receptor model, obtained for Denver, USA. Major discrepancies were reported where the emission inventory attributed 45% of the $PM_{2.5}$ emissions to fugitive dust sources, and 80% of the mobile source emissions to diesel exhaust. Conversely, the CMB receptor model indicated that the dust contribution was only 16% and that diesel was responsible for approximately 25% of the mobile source contributions.

⁶⁶ The USEPA emission factors used for residential wood combustion are usually limited to filterable emissions, but some include condensables (Scott and Gunatilaka, 2004). Condensables are also partly accounted for in the industrial and motor vehicle emission factors, but these will not account for the formation of secondary particles from SO_x and NO_x gases (USEPA, 1995).

⁶⁷ A real-life wood burner emissions study has suggested that the emission factor for low emission wood burners ($3 g/kg$) is too low by up to a factor of 4 or 5 (Scott, 2005b), the industrial emission factors are largely based on USEPA data (may not be representative of Christchurch sources and fuels), and the motor vehicle emission factors may be dated (these were derived from tests conducted prior to 1998). The USEPA recommends the use of locally-derived emission factors, where possible (USEPA, 1995).

Issues associated with the box model discussed here relate to its simplicity, where the spatial variations in emission sources, concentrations, deposition and meteorology are ignored. Also, it does not account for the physical and chemical transformation of contaminants from point of discharge to measurement at the receptor site and assumes that the meteorological conditions specified in the model represent those of the time period of concern. However, the uncertainty issues are not limited to the box-modelled and emission inventory estimates, as issues relating to unresolved sources and the high error associated with the motor vehicle regression coefficients apply to the receptor modelling results. Limitations associated with the receptor modelling are discussed in the following chapter.

Because of these factors, the box-modelled emission inventory and receptor-modelled estimates obtained by this study cannot realistically be expected to be the same. While the receptor-modelled results are unlikely to be entirely representative of the sources and their contributions to PM_{2.5} measured at Coles Place, the results are potentially more accurate than those provided by the box-modelled emission inventory data. The receptor model directly attributes source contributions to measured concentrations at the receptor site,⁶⁸ and accounts for the secondary and natural components.

Regardless of the variations between methodologies, both methods identified wood combustion/residential heating as the main source of wintertime PM_{2.5}, and indicated that the contributions were of similar magnitudes. The receptor model demonstrated that wood combustion was important on an average winter's day (79%), average high pollution day (87%) and on the maximum PM_{2.5} day (92%).

However, to obtain a complete picture of the impact of primary emission sources identified by the receptor model on PM_{2.5}, potential contributions to secondary particulate sources (i.e. secondary particulate and aged aerosol) must be considered. In this regard, contributions from wood combustion, marine aerosol and motor vehicles will be greater than that suggested in Table 11.4. These sources also discharge OC, NO_x and SO_x emissions, which react in the atmosphere to form secondary organics, nitrate, sulphate and ammonium compounds. The secondary particulate and aged aerosol source contributions are most likely dominated by compounds such as (NH₄)₂SO₄, NH₄HSO₄, Na₂SO₄, NH₄NO₃, and NaNO₃. Nitrate is formed from the oxidation of NO to NO₂ and further oxidised to HNO₃. This reacts with NH₃ gas (from animal urine and biological activity of soils) to form NH₄NO₃. Sources of NO_x gases in Inner Christchurch, as identified by the emission inventory include motor vehicles (86% of total NO_x), industrial and commercial activities (8%) and residential heating (7%). Nitrate was the most important species present in the secondary particulate factor

⁶⁸ Estimated average PMF mass for the high pollution days (63 µg m⁻³) is almost identical to PM_{2.5} concentrations (64 µg m⁻³) and in this regard contributions to PMF mass and PM_{2.5} are essentially the same.

and, therefore, it is probable that motor vehicles were responsible for the majority of contributions from this source. If it is assumed that motor vehicles were solely responsible for the secondary particulate estimates, motor vehicles could potentially contribute up to 3% of maximum $PM_{2.5}$, 8% of $PM_{2.5}$ on high pollution days and 13% on average over winter.

The aged aerosol source included some particles of soil origin (Section 10.5) but appeared to be dominated by Na_2SO_4 . Sulphate is formed from the oxidation of sulphur gases to SO_2 . This reacts with NH_3 gases to form $(NH_4)_2SO_4$ or NH_4HSO_4 , or with NaCl in marine environments to form Na_2SO_4 . The source sector mostly responsible for SO_x emissions, according to the emission inventory, is industry and commerce (70%). Motor vehicles were also significant sources of these gases with an estimated contribution of 23% (Scott and Gunatilaka, 2004). Sulphur gases may also be derived from phytoplankton and algae in marine environments which can also form Na_2SO_4 when reactions with NaCl occur (Meszaros, 1999; Hobbs, 2000; Claes *et al.*, 1998). The absence of carbon in the profile suggested that a non-combustion source may be responsible for the precursor gases. This is further supported by the meteorological data which indicated that easterly winds were important features of aged aerosol events. However, there was a negative correlation between the motor vehicle and aged aerosol source suggesting that under certain meteorological conditions, sulphur from diesel vehicles could potentially react with other contaminants in the atmosphere to form Na_2SO_4 . For example, under warm, easterly conditions, NaCl of marine origin may react with SO_x emissions (these could be from a variety of sources including marine, motor vehicle and industrial) to form secondary sulphate. As there were multiple sources of SO_x it was not possible to attribute aged aerosol contributions to a single source sector with a reasonable degree of certainty.

11.4 Summary

The determination of the proportion of $PM_{2.5}$ accounted for by the elemental species measured, and by the sources resolved by the receptor modelling, is an important component of the analysis. If the measured chemical species only account for a low proportion of the $PM_{2.5}$ mass, then the receptor modelling results will only partially explain $PM_{2.5}$. An assessment was conducted where the mass was "reconstructed" using conversion factors, and by summing the source contributions determined by the receptor model. Using the conversion method (with overestimated data adjusted to 100% of mass), approximately 79% of summertime $PM_{2.5}$ and 74% of wintertime $PM_{2.5}$ on average could be explained by the chemical species measured (76% overall). The ability of the receptor model to account for most of the chemical measurements was also assessed. Like that demonstrated for the conversion method, mass was underestimated by the PMF receptor model. However, as a good relationship was evident between explained PMF mass and measured $PM_{2.5}$ ($r^2 = 0.9$), it was assumed that a linear combination of the source contributions would be responsible for the entire $PM_{2.5}$ mass. On this basis, 87% of summertime and 94% of wintertime mass was accounted for by the modelling (92% overall), indicating that the model results explain most of the $PM_{2.5}$ in Christchurch. The unexplained mass

component was also investigated by examining its relationship with the elemental measurements and the sources resolved. It appeared that the strongest associations were with the wood combustion source and its chemical constituents. This may be related to the OC concentrations, in particular, as unexplained mass has been linked to OC measurements in other studies.

The receptor model results were evaluated against box-modelled emission inventory data to determine whether the sources and the magnitude of the contributions were similar. Key differences were the sources resolved (the emission inventory only quantified anthropogenic primary emission sources and the receptor modelling did not resolve an industrial factor), and relatively minor differences in the contributions from wood combustion/residential heating and motor vehicles. There were uncertainties associated with both methods and some differences should be expected.

Nevertheless, both methods clearly identified wood combustion/residential heating as the main source of peak $PM_{2.5}$ emissions, adding to the "weight of evidence" regarding source identification in Christchurch. The receptor model also quantified contributions from natural and secondary particulate sources, the precursors of which are derived from a variety of primary emission sources. Motor vehicles were most likely responsible for the precursor gases that react to form nitrate (the key secondary particulate species), and possibly a combination of marine, soil, industrial, and motor vehicles were responsible for the precursors leading to the aged aerosol contributions (mostly Na_2SO_4).

Chapter 12: Summary and conclusions

The following outcomes were successfully achieved by this study:

- PM_{2.5} concentrations were measured in Christchurch using a filter-based method.
- The chemical composition of PM_{2.5} was determined on a seasonal basis.
- A source apportionment method that quantified contributions to 24-hour average PM_{2.5} concentrations, taking into account natural sources and day-to-day variations, was investigated and trialled.
- Winter and summertime sources of PM_{2.5} were characterised, and their contributions to 24-hour concentrations in Christchurch quantified.
- A case for including receptor modelling as an air quality management tool is presented (this chapter).

This chapter summarises the key findings in relation to the study objectives, and outlines a justification for including receptor modelling in air quality management programmes.

12.1 Key findings

12.1.1 Fine particle concentrations in Christchurch

Fine particles were seasonally distributed, with higher concentrations evident during the winter months. A maximum 24-hour average PM_{2.5} concentration of 96.3 µg m⁻³ was measured on 22 May 2002, with a median wintertime concentration of 20.9 µg m⁻³. In summer, the maximum 24-hour average measurement was 28.3 µg m⁻³ with a median of 5.5 µg m⁻³. Routine measurements of PM₁₀ indicated that the maximum PM_{2.5} concentration (as indicated by a high volume sampler) measured during the study was unlikely to be the highest in 2001/2002.⁶⁹ The 24-hour average PM₁₀ concentration on 22 May 2002 was 111 µg m⁻³, whereas the maximum concentration measured that year was 252 µg m⁻³ (19 July 2002). High concentrations were also recorded during short-term studies conducted in 2001 and 2004, with maximum 24-hour averages of 143 µg m⁻³ (Scott, 2002) and 146 µg m⁻³, respectively (as measured during the OC/EC investigation).

The PM_{2.5} measurements were evaluated against the MfE monitoring value for PM_{2.5} (25 µg m⁻³, 24-hour average). The monitoring value was exceeded on 45% of wintertime sampling days, and if all available data had been retained in the analysis, a greater number of exceedences would have occurred. High concentrations were not just limited to the winter period as there were two exceedences of the MfE monitoring value during March 2002. Outdoor burning sources were most

⁶⁹ 20 samples were invalidated during the study due to particle overloading and filter blockage issues.

likely responsible for elevated concentrations at that time. Overall, the data indicate that the community of Christchurch is exposed to elevated concentrations for extended periods of time.

12.1.2 Chemical characterisation of fine particles and seasonal variations in Christchurch

The major elemental constituents of $PM_{2.5}$ were OC_{mass} , BC, EC, sulphate, nitrate, sodium, chlorine and sulphur.⁷⁰ In winter, particles were predominantly of combustion or secondary particulate origin. Of those species that were most abundant in winter, median 24-hour average concentrations were OC_{mass} ($5.4 \mu g m^{-3}$), EC ($5.1 \mu g m^{-3}$), BC ($5.2 \mu g m^{-3}$), nitrate ($0.7 \mu g m^{-3}$), sulphate ($1.1 \mu g m^{-3}$), ammonium ($0.3 \mu g m^{-3}$), and potassium ($0.2 \mu g m^{-3}$). Chemical species associated with marine environments, sodium and chlorine, were more abundant in summer. Median summertime concentrations for these species were $0.5 \mu g m^{-3}$ for chlorine and $0.8 \mu g m^{-3}$ for sodium. The seasonal variations observed were related to changes in emission sources and meteorological conditions. Sulphur was the only major species that did not exhibit any seasonality. Maximum concentrations of the key chemical species were OC_{mass} ($22.9 \mu g m^{-3}$), BC ($22.7 \mu g m^{-3}$), EC ($27.3 \mu g m^{-3}$), sulphate ($2.7 \mu g m^{-3}$), chlorine ($2.5 \mu g m^{-3}$), sodium ($2.4 \mu g m^{-3}$), nitrate ($2.3 \mu g m^{-3}$), sulphur ($1.3 \mu g m^{-3}$), ammonium ($1.2 \mu g m^{-3}$) and potassium ($0.9 \mu g m^{-3}$).

While OC_{mass} , EC and BC were the most abundant species, there were issues associated with the measurement of these compounds. OC and EC were measured continuously using an R&P Series 5400 ambient carbon particulate monitor, and BC by light reflection/transmission. A non-default temperature setting was used by the Series 5400 and it was suspected that OC_{mass} was being underestimated and EC overestimated by the analytical technique used. This was confirmed by a separate investigation conducted during the winter of 2004. The study compared OC and EC measurements provided by the Series 5400, set at a OC/EC differentiation temperature of $230^{\circ}C$; results were evaluated against those provided by the filter-based TOR analytical method.

Fine particle concentrations were higher in 2004 ($146 \mu g m^{-3}$) than those sampled in 2001/2002, which resulted in higher carbon concentrations. The TOR concentrations for TC ranged from $1.1 \mu g m^{-3}$ to $97.8 \mu g m^{-3}$, with a median of $17 \mu g m^{-3}$. OC was more abundant than EC, ranging from $0.6 \mu g m^{-3}$ to $76.9 \mu g m^{-3}$, with a median of $12.3 \mu g m^{-3}$. EC ranged from $0.5 \mu g m^{-3}$ to $21 \mu g m^{-3}$, with a median of $4.8 \mu g m^{-3}$. The 24-hour concentrations provided by TOR indicated that mean wintertime values were similar to those measured in other parts of the world, although maximum concentrations were substantially higher in Christchurch than those measured in large cities such as Los Angeles. On 20 July 2004, when $PM_{2.5}$ was greatest ($146 \mu g m^{-3}$), OC_{mass} comprised 74% and EC 14% of the mass, with a TC contribution of 88%. The 2004 investigation demonstrated that OC was more abundant than EC, carbon comprised the majority of $PM_{2.5}$ mass on high pollution days,

⁷⁰ The OC_{mass} ($OC \times 1.4$) and EC concentrations discussed in this section are not representative of those measured using the more widely used TOR method. This is discussed later.

the two methods used for providing the carbon measurements did not produce equivalent results, and that the difference between methods was statistically significant. The response to these findings with regard to the receptor modelling is discussed later in the chapter.

12.1.3 Investigation and trial of a receptor model for source apportionment purposes in Christchurch

Prior to conducting a source apportionment of Christchurch PM_{2.5} data using a receptor model, a Spearman R correlation analysis was undertaken to provide an initial indication of elemental groupings and potential sources. The strongest associations were found between the carbon compounds, iron, potassium and zinc. Secondary particulate species were also significantly correlated (e.g. ammonium and nitrate had a coefficient of 0.85). On a seasonal basis, the greatest summertime associations were between the main constituents of marine aerosol, sodium, chlorine, calcium and magnesium, and in winter, between combustion and secondary particulate species. Sulphur was associated with different species, depending on season, with the strongest links to secondary particulate compounds such as sulphate in summer, and with those of combustion origin in winter. This suggests that during the warmer months of the year, sulphur is predominantly present in a secondary particulate form, but in winter, as primary sulphur.

Following a review of receptor modelling research conducted in New Zealand and elsewhere, the PMF multivariate receptor model was selected for investigation. The PMF model, which conducts a least-squares analysis, was applied to the dataset to characterise the key sources of PM_{2.5}. This particular model was preferred to other factor analytical techniques as the data are not normalised (factor scores and loadings are provided in real units) and measurement uncertainties are taken into account during the modelling process. Unlike methods such as PCA, the results may be used directly to assemble source profiles and quantify relative source contributions. This receptor model was investigated to determine its ability to provide alternative source attribution information to that provided by emission inventories, and its potential as a tool for monitoring effectiveness of plan strategies.

Initially, the analysis was undertaken using the OC_{mass} data from the Series 5400 and BC measured by light reflection/transmission (the investigation of OC and EC was not undertaken until later in the study). A PCA was conducted to provide a quick overall indication of potential factors. Most of the data variance was accounted for in the first factor, even after rotation, and only two sources were sufficiently resolved from the others (marine aerosol and secondary particulate). The PMF receptor model was subsequently applied to the data and five preliminary factors were resolved. These were identified as wood combustion, motor vehicles, marine aerosol, secondary particulate and aged aerosol.

However, the use of OC_{mass} and BC as separate species in the dataset led to the generation of potentially misleading factors.⁷¹ An investigation of OC and EC in 2004, confirmed earlier suspicions that the carbon measurements provided by the Series 5400 analyser in 2001/2002 did not adequately differentiate between OC and EC. In this regard, it was inappropriate for OC_{mass} to be included as a separate variable in the receptor modelling. As a good relationship was established between TC measured by the Series 5400 and the TOR methods (although the Series 5400 underestimated TC by approximately 10%), the optimal solution was to combine the 2001/2002 OC_{mass} and EC data to provide measures of TC_{mass}. This allowed most of the elemental constituents measured in 2001/2002 to be included in the modelling, and prevented potential misinterpretation of the resolved factors. The final dataset used for the modelling consisted of 15 chemical species, including TC_{mass}.

The PMF receptor model was applied to the final dataset and operated via an initialisation file. Various parameters were adjusted, including the number of factors, until an acceptable Q-value (goodness of model fit) was achieved. Multiple PMF runs were required (trial-and-error) to optimise these parameters. Five factors were eventually selected, and the modelling repeated from different starting points to obtain the best solution. The theoretical Q-value for a 15 x 159 concentration matrix was estimated to be between 1515 and 2385.⁷² The Q-value obtained by the modelling was 1420 and the most central solution (f-peak=0) was used, as there was very little rotational freedom evident in the G-Factors. Chemical profiles for the final solution were derived directly from the F-Factor matrix (factor loading matrix). The five factors resolved were identified as wood combustion, motor vehicles, marine aerosol, secondary particulate and aged aerosol. The G-Factor matrix (daily factor scores) components were regressed against gravimetric PM_{2.5} measurements using MLR. The regression coefficients were then multiplied by the daily factor scores to calculate daily source contributions to PMF mass.⁷³

The PMF receptor model groups elemental species into factors (source profiles) and determines source strength on a daily basis, but cannot identify the factors. This analysis is undertaken by the modeller. The quality of the source identification was assessed by reviewing the chemical composition of each source, particle morphological characteristics, and temporal patterns in

⁷¹ The ratio of OC to EC is often used in the interpretation of resolved factors. This was inappropriate in this instance as the OC_{mass} and BC measurements were collected by two different instruments and OC_{mass} was underestimated. Consequently, these measurements did not accurately represent the proportional abundance of OC_{mass} and EC in Christchurch, and an interpretation based on the ratios would be inaccurate.

⁷² One definition of the theoretical Q value is: $Q = n \times m - p \times (n + m)$ where p is the number of factors, n is the number of samples and m is the number of species included in the analysis (Phil Hopke, Clarkson University, Potsdam, USA, *pers. comm.*). On this basis, the theoretical Q value would equal 1515. This differs from that indicated in Paatero (2000b), where it is suggested that the theoretical Q value is approximately equal to the number of data points in the concentration matrix. As it is uncertain which rule applies, the theoretical Q is assumed to be between 1515 and 2385.

⁷³ PMF mass was not always identical to PM_{2.5}, as PMF sometimes over and underestimated the mass contributions. If it is assumed that overestimated mass was equal to 100% of PM_{2.5}, then on average PMF represented 92% of PM_{2.5}.

contaminant concentrations and meteorology. The chemical profiles of the sources identified were very similar to those indicated elsewhere; and seasonal patterns in the source contributions, particles present on the SEM micrographs, and the meteorological conditions were consistent with those expected of each source.

The extent to which the PMF receptor model results actually explained $PM_{2.5}$ in Christchurch was also evaluated. The amount of $PM_{2.5}$ mass accounted for by the elemental measurements and the sources identified, and the model's ability to explain the individual elemental concentrations were determined. When the elemental mass was reconstructed prior to modelling using standard conversion equations, approximately 76% of average $PM_{2.5}$ was accounted for (when overestimated mass was adjusted to 100% of mass). The matrix of scaled residuals output by the model was reviewed and, with the exception of some outlier values, most chemical species were modelled effectively (with residuals between -2 and 2).⁷⁴ The amount of $PM_{2.5}$ accounted for by the PMF mass (i.e. sum of the source contributions) was, like the converted reconstructed mass, underestimated. However, as a good relationship existed between PMF mass and $PM_{2.5}$, it was assumed that a linear combination of the source contributions was responsible for all $PM_{2.5}$. In this instance, the results of the study provide an excellent representation of $PM_{2.5}$ in Christchurch (approximately 92% of average $PM_{2.5}$ was explained by the PMF receptor model). An investigation of the unexplained component indicated that unexplained mass may be associated with the wood combustion source, and its elemental constituents.

12.1.4 Key summer and wintertime sources of fine particles in Christchurch

The five sources identified by the PMF receptor model were wood combustion, marine aerosol, motor vehicles, secondary particulate and aged aerosol. The wood combustion source was characterised by the presence of carbon, potassium, nitrate and chlorine; marine aerosol by sodium, chlorine and magnesium; motor vehicles by carbon, soil-related species (silicon and magnesium), and metals (nickel, aluminium and zinc); secondary particulate by carbon, nitrate, ammonium and sulphur; and aged aerosol by sulphur, sodium, and soil-related species (silicon, magnesium, iron, potassium and aluminium). Daily 24-hour average contributions from all sources, with the exception of the aged aerosol source, exhibited seasonality characteristics. Wood combustion, secondary particulate and motor vehicles were more significant during the winter months, whereas the marine aerosol contributions were usually greatest in summer. These variations were linked to seasonal differences in source discharges, and/or in meteorology. In the wintertime, temperature inversions trap emissions from residential heating and motor vehicles. The contaminants accumulate and react in the atmosphere, leading to high secondary particulate concentrations. Conversely, residential heaters

⁷⁴ Paatero (2002b) suggested that if the correct number of factors is selected, and if the errors are appropriately allocated, the residuals should be within -2 and 2 .

are rarely used in the summer and strong northeasterly winds, typical of summertime meteorology, dilute any emissions present and transport marine aerosol across Christchurch.

Wood combustion events were typified by high PM_{10} and $PM_{2.5}$ concentrations (peaking overnight), temperature inversions and calm conditions. Motor vehicle contributions were greatest when temperature inversions coincided with peak-hour traffic, and generally occurred under calm conditions and low temperatures. The conditions that led to the highest secondary particulate contributions were low wind speeds, higher temperatures (compared to those evident for the other sources), and relatively high NO and NO_x concentrations during the morning period. Marine aerosol, unlike wood combustion, secondary particulate and motor vehicles, was usually greatest in the summer months, although some wintertime peaks were found. High wind speeds were typical of marine aerosol events and winds were from an easterly, and sometimes southwesterly, direction. The final source, aged aerosol, which was consistently present throughout the sampling period, was characterised by low wind speeds, and winds were usually from an easterly direction with a late change to lighter west to southwesterly winds, reasonably high relative humidity and very warm temperatures.

During the 2001/2002 summer, aged aerosol was the greatest source of average PMF mass (31%). This was followed by wood combustion (26%), marine aerosol (21%), secondary particulate (12%) and motor vehicles (10%). However, when summertime PMF mass was greatest (8 and 27 March 2002),⁷⁵ wood combustion contributed to 53% of mass, followed by aged aerosol (22%), motor vehicles (11%), secondary particulate (10%) and marine aerosol (4%). In winter, wood combustion was responsible for 79%, on average, of PMF mass, and secondary particulate for 9%, aged aerosol for 5%, motor vehicles for 4% and marine aerosol for 3% of PMF mass. When wintertime mass was greatest (22 May 2002), wood combustion contributed to 92%, aged aerosol to 3%, marine aerosol to 2%, secondary particulate to 2% and motor vehicles to 1% of PMF mass.

The relative source contributions derived by the receptor model were evaluated against those estimated using box-modelled emission inventory data (2002), which represented contributions to peak $PM_{2.5}$. Key differences were the number and type of sources resolved and minor variations in the relative contributions from wood combustion/residential heating and motor vehicles. The emission inventory only quantified discharges from primary anthropogenic sources including residential heating, motor vehicles and industry. The receptor model resolved a broader wood combustion source, which included outdoor burning and industrial wood-fired boilers, as well as secondary (secondary particulate and aged aerosol) and natural sources (marine aerosol). Although the wood combustion source also included contributions from outdoor burning and wood-fired boilers, these were unlikely to be significant contributors to the peak $PM_{2.5}$ event (22 May 2002). Despite the

⁷⁵ NB: the maximum summertime $PM_{2.5}$ concentration in 2001/2002 was $28 \mu g m^{-3}$, which occurred on 28 March 2002. PMF mass was substantially underestimated on this day ($10 \mu g m^{-3}$), highlighting issues associated with contributions estimated during the summer months.

differences between methodologies, and the amount of $PM_{2.5}$ actually accounted for, both methods clearly identified wood combustion/residential heating as being by far the main source of wintertime $PM_{2.5}$ (92% by receptor model and 89% by box-modelled emission inventory data).

However, the study also demonstrated that not insignificant quantities of $PM_{2.5}$ were from secondary particulate (including aged aerosol) and marine aerosol sources. These also need to be identified and quantified when determining relative source contributions to $PM_{2.5}$. This study could not definitively establish the sources responsible for the secondary particulate and aged aerosol contributions. Nevertheless, as NO_x and nitrate were elevated on high secondary particulate days, it was suggested that motor vehicles, the major anthropogenic source of NO_x emissions (a precursor of nitrate), could be responsible for the bulk of the secondary particulate contribution. Conversely, the aged aerosol source, which consisted of soil and Na_2SO_4 , could not be reasonably attributed to a specific, single source.

12.1.5 Limitations and strengths of PMF receptor modelling

This study has demonstrated that the receptor model used (PMF) was particularly effective at explaining $PM_{2.5}$ in Christchurch. The five factors resolved by the model; wood combustion, motor vehicles, aged aerosol, secondary particulate and marine aerosol, were consistent with other observations and provided independent verification that residential heating is the greatest contributor to wintertime particle concentrations in Christchurch. Thus, the research provides greater confidence concerning the identification of the problem sources and the strategies adopted, and adds to the "weight of evidence" that underlies the strategies adopted in Environment Canterbury's proposed plan. The receptor model also provided additional information concerning the natural and secondary particulate components of $PM_{2.5}$, and estimated relative source contributions on a daily basis. In this regard, the PMF receptor model would be an effective tool for monitoring the effectiveness of control strategies over time.

However, there were a number of limitations/issues associated with this study and the methodology adopted. The source apportionment results were limited to the receptor site (Coles Place, St Albans) and the time period measured. Therefore, the results were likely to be representative of an inner Christchurch suburb, but not necessarily of the entire Christchurch metropolitan area. Also, the presence of strong temperature inversions over much of the wintertime period posed some problems for the modelling. First, high particulate loadings led to filter blockages and the subsequent invalidation of data from those days. The results therefore are not necessarily representative of the maximum $PM_{2.5}$ concentration in 2002. Second, strong inversion conditions may have contravened one of the key receptor modelling requirements, where the effect of processes such as temperature inversions on emissions must be less than processes that affect individual sources (Seinfeld and Pandis, 1998). This may have caused difficulties in resolving sources on certain days.

The receptor model was able to resolve a secondary particulate factor, thus improving the current understanding of secondary particulate contributions to $PM_{2.5}$ in Christchurch. However, it was not able to determine which sources were responsible for the generation of the secondary particulate precursors. Information from other resources, such as emission inventories, were needed to accommodate this short-fall. In addition, the model appeared to identify the main sources of $PM_{2.5}$, but did not resolve any industrial, soil or diesel vehicle factors. This was either because none of these sources actually impact on the receptor site, or that their contributions were very minor. The quality of the modelling also varied by season as a lower proportion of maximum summertime $PM_{2.5}$ was accounted for by the elemental measurements than in winter. More general limitations associated with receptor modelling relate to the difficulties in determining the appropriate number of factors to select, and the requirement for large datasets for successful analyses to be conducted.

The PMF receptor model itself was more difficult to use than standard methods incorporated into statistical programmes, such as PCA. The preparation of the uncertainty matrix was not straightforward and was relatively time consuming. However, these disadvantages were far outweighed by the additional benefits gained by using this model. Factor loadings and scores were provided in real units, which allowed source apportionment to be conducted directly and assisted in the evaluation of the source profiles (e.g. elemental ratios could be compared to source measurements or with profiles undertaken in other airsheds elsewhere). The model took measurement uncertainty into account, avoided distortion of the analysis by outliers, did not generate negative factor loadings or scores, included a goodness of model fit function to assist with factor selection, allowed rotation, and provided a residual matrix that assisted in the determination of model quality.

This study has demonstrated that receptor modelling is a particularly effective source attribution tool and it is strongly recommended that, in those areas where air quality is an important issue, consideration is given to permanently including receptor modelling in regional air quality management programmes. In summary, receptor models may assist with the following:

- Provide greater confidence in the identification of the main sources contributing to PM and thus increase confidence in the appropriateness of air quality measures.
- Provide information on the contributions from sources that cannot be controlled or readily accounted for by standard emission inventory techniques (e.g. marine aerosol) and determine the potential impact of secondary particulate on $PM_{2.5}$ concentrations.
- Monitor the effectiveness of plan strategies and track improvements over time.

These are issues that are faced by air quality regulators throughout New Zealand. The ability of receptor models to deliver these outcomes is discussed further in the following section, in the context of the situation in Canterbury.

12.2 Receptor modelling as an air quality management tool

The regulatory authority responsible for managing discharges to air in Christchurch, Environment Canterbury, currently has a proposed Canterbury Natural Resources Regional Plan – Air Quality. The measures included in the proposed plan specifically target the main source of PM_{10} and $PM_{2.5}$, residential heating, as determined by emission inventory (and box modelling). The proposed plan sets out air quality objectives for Canterbury. These objectives are given further weight by the introduction of a NES for PM_{10} by the MfE. According to the NES, regional authorities in non-complying areas will not be able to issue resource consents for any activity that may cause emission loads to increase above a modelled downward trend-line. MfE is also considering whether or not an annual PM_{10} standard should be developed.

The appropriateness of the measures contained in Environment Canterbury's proposed plan are debated by some members of the community who are convinced that motor vehicles, rather than residential heating, are the main source of wintertime PM in Christchurch. This misconception must be addressed, as community support and action is central to the success of many of the strategies in the proposed plan. To achieve the level of community support required, regulators need to demonstrate a robust and complete understanding of sources and their contributions to local air quality problems. This study has addressed this concern and corroborated emission inventory findings that in Christchurch, residential heating is the main source of wintertime emissions (contributing 79% on average to wintertime $PM_{2.5}$).

The introduction of the NES for PM_{10} , and the possibility that an annual average standard is introduced in the future, are important considerations for regulators in New Zealand. Greater confidence is needed in determining the amount of reduction that may feasibly be achieved by targeting residential heating emissions. Improved knowledge of the relative impact of secondary particulate, and its potential sources, is also required, as current strategies may not sufficiently address these sources. Additional control strategies may be needed to control precursor emissions (NO_x in particular) from sources such as motor vehicles. In addition, the amount of PM that cannot be controlled by emission strategies needs to be established. These sources may become increasingly important as the NES and NRRP air quality deadlines approach in 2012/2013 and the relative impact of wood combustion sources reduces. The receptor model investigated during this study was able to resolve two secondary particulate sources (aged aerosol and secondary particulate) and a natural source (marine aerosol). The contributions to summer and wintertime averages and maximum PM concentrations were quantified (e.g. secondary particulate constituted 9%, aged aerosol - a mixed secondary particulate and natural source - 5%, and marine aerosol 3% of average wintertime $PM_{2.5}$). However, it was more difficult to accurately quantify sources contributing to summertime $PM_{2.5}$.

Air quality regulators in New Zealand can learn from the experience of those in the US, where early emission control strategies were developed on the basis of emission inventory proportional rollback models, and dispersion modelling analysis of source contributions (Core, 1991). This is not dissimilar to the approach adopted for Christchurch, except that emissions were inserted into a simple box model to determine the relative contributions to concentrations. Core (1991) indicated that the control strategies developed on this basis had limited success, as not all particulate sources could be quantified by emission inventory (e.g. secondary particulate). However, integral to the issues experienced in the US was that most inventories only quantified emissions on an annual basis, which posed difficulties for modelling individual days, and because secondary particulate was a major contributor to $PM_{2.5}$. In response to these concerns, a receptor modelling programme was initiated in Portland, Oregon. Interestingly, this programme provided the first indication that residential wood burning was a major source of $PM_{2.5}$ in Portland on worst-case winter days (40%). These findings led to the development of new control strategies, the adoption of the Oregon Woodstove Certification Programme and provided the basis for the USEPA's national wood stove certification programme (Core, 1991).

These experiences demonstrate the importance of adopting more than one source attribution method. The present study has shown that receptor modelling can provide a good overall assessment of key sources and their contributions to $PM_{2.5}$ concentrations. As this research confirmed that residential heating is the main source of wintertime $PM_{2.5}$ in Christchurch, it is unlikely that NRRP emission control strategies will be amended in the short-term. Nevertheless, this type of research is needed to confirm whether or not this is the case for other parts of New Zealand, where a different mix of source types is anticipated (e.g. Auckland).

The final key benefit associated with including receptor modelling in major air quality management programmes relates to its potential for tracking progress towards achieving air quality targets. In doing this, those authorities that have plans in place (or proposed) to address PM will need to:

- demonstrate that PM concentrations are decreasing,
- demonstrate the adequacy of control strategies,
- attribute declining concentrations to the different source sectors,
- quantify the proportion of PM from natural sources (e.g. marine aerosol and soils), and
- quantify the secondary particulate component of PM.

Currently, the methods routinely adopted for demonstrating declines in concentrations and tracking changes in source contributions over time are air quality monitoring and emission inventories. While these are both important tools, additional work is required to attribute declines in concentrations to the different source sectors. The emission inventory loading estimates must be transformed using

models into concentrations to allow relative contributions to be determined. The resulting concentrations are dependent on the meteorological variables included in the modelling. Those included in Environment Canterbury's box model, for example, are only representative of the highest pollution days. It is also difficult to accurately account for natural source and secondary particulate contributions by emission inventories.

Receptor modelling is a complementary technique that should be used in conjunction with, rather than as an alternative to, routine monitoring and emission inventories. This study demonstrated that the PMF receptor model could identify the main sources of PM_{2.5} in Christchurch, and enabled the relative contribution of the different sources to daily concentrations, and contributions from both natural and secondary sources to be determined. This technique required the collection of speciated data (thus providing information on chemical species otherwise not quantified), and allowed seasonal variations in sources and their contributions to be established. It quantified the amount of PM that cannot be controlled by management strategies - that is, the natural component. This is important, as the natural component should be considered when calculating the reduction required in anthropogenic emissions for air quality management purposes. Likewise, secondary particulate contributions are also essential considerations, as the sources responsible may differ to those being targeted in current strategies. If these are not the same, then secondary particulate could potentially increase in significance. Tracking this over time will be necessary and may require the introduction of new control strategies. A greater understanding of variations in sources, and their contributions across a year, may also be needed if MfE eventually introduces an annual PM₁₀ standard.

Routine monitoring is still vital, as it allows daily contaminant concentrations to be evaluated against air quality standards and guidelines, and provides diurnal trends in contaminants and meteorology (important for understanding high pollution events). Similarly, emission inventories are needed to demonstrate emission reductions, provide spatial emission data for airshed modelling purposes, quantify emissions from sources that may not be resolved by receptor models (e.g. industry), assist with the development of air quality strategies by providing information on individual sources within each category (so we know what to target), and to provide information on the key sources responsible for the precursors of secondary particulate (e.g. NO_x and SO_x).

The relativity between the various information gathering components, including receptor modelling, in air quality management programmes is presented in Figure 12.1. Other frameworks include those suggested by Watson *et al.* (2002) and Pace (1991). A proposed source apportionment study design is provided in Appendix 11.

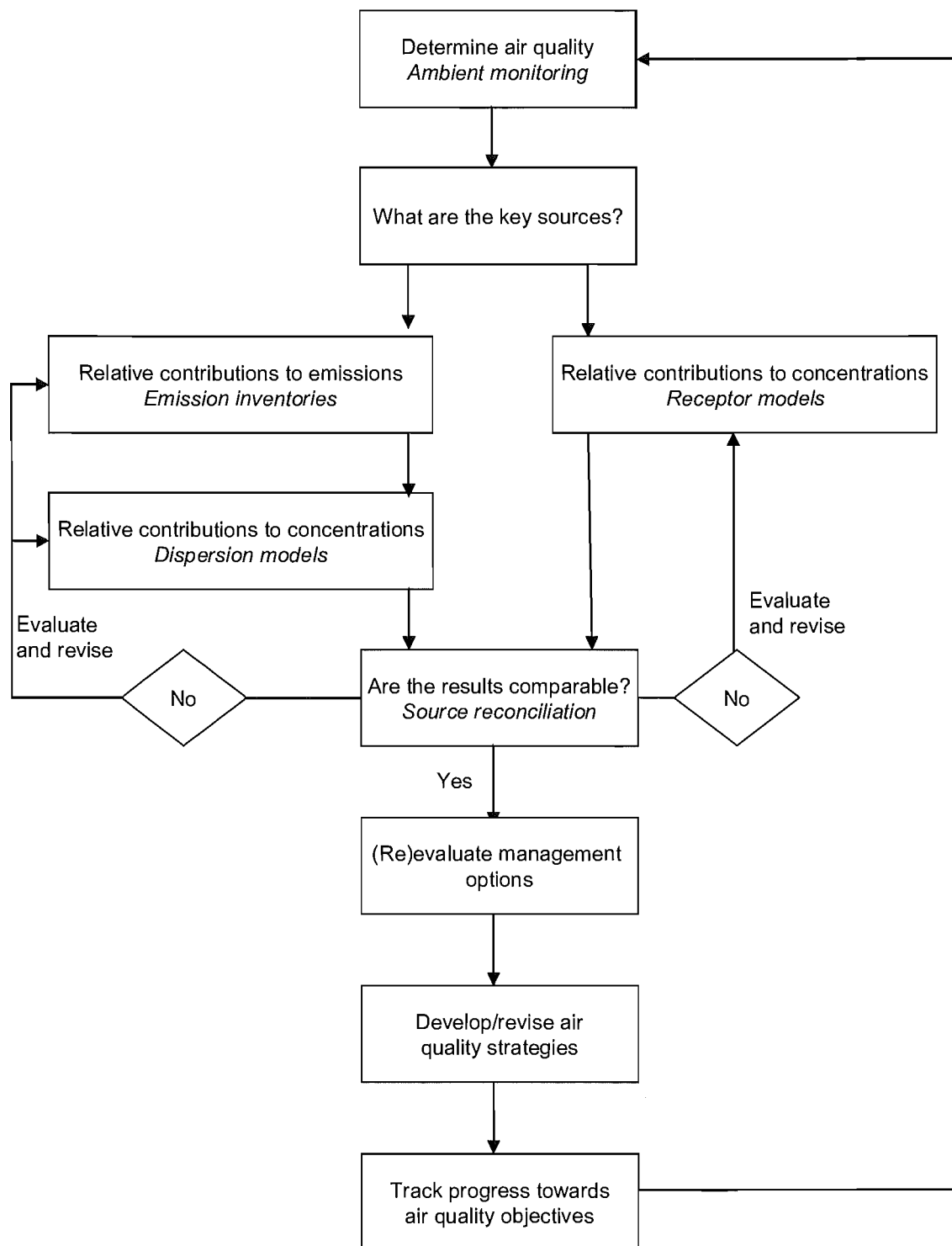


Figure 12.1 Receptor modelling and its place in the air quality management framework.

12.3 Suggestions for future work

There is a variety of work that could be conducted to further refine the findings of this study and to advance source apportionment in New Zealand. One key area of uncertainty is the relative source contributions in summer. It was more difficult to account for PM mass by the elemental

measurements at that time of year and it would be useful to determine whether the relative contributions reported are representative. In addition, the aged aerosol source, which appeared to represent a combined soil and Na_2SO_4 source, requires further investigation. Contributions from this source were not insignificant and by 2012/2013 may become relatively more important. Also essential, is the development of a methodology for calculating the errors or uncertainties associated with the source contribution estimates provided by PMF. This was not conducted for this research as it was unclear how these could reliably be calculated to incorporate all areas of uncertainty.⁷⁶ Nevertheless, it is an important area that needs to be addressed.

An area of potential research in Christchurch relates to secondary particulate and its precursors. Like aged aerosol, this could become an increasingly important component of $\text{PM}_{2.5}$ in future years. Current understanding of sulphate, nitrate and ammonium and their interactions with other chemical compounds in Christchurch is limited. In particular, further work is needed to determine particle composition and behaviour during the early morning period. This should address the precursors of these compounds, how and when the compounds are formed (i.e. interactions of NO , NO_x and SO_x , overnight nitrate formation and any links to particles emitted overnight), the influence of meteorological variables such as temperature and humidity on secondary particulate formation and growth, and should include measures of particle size to determine whether the morning peak is dominated by freshly formed particles or aged particles.

The measurement of OC and EC continues to be an issue in Christchurch. Clearly, the Series 5400 operated at 230°C did not provide measures that could be compared with studies elsewhere. Further work is needed to determine which temperature setting provides data most representative of TOR equivalent OC and EC,⁷⁷ or a different measurement and analytical method investigated.⁷⁸ Associated with the measurement issues is the conversion factor used to account for the unmeasured elemental species present in organic compounds. Further research is required to determine the conversion factor applicable to summertime and wintertime data, as it is likely that the factor will vary depending on the emission sources present.

Some PMF studies have attempted to apply various backward trajectory analysis techniques to determine the physical origin of the sources resolved. The source contribution function and the conditional probability function, for example, have been used in several PMF receptor modelling

⁷⁶ The PMF receptor model presently provides uncertainty estimates for the G and F-Factors. However, Pentti Paatero (Helsinki, Finland, *pers. comm.*) indicates that these estimates ($G_{\text{std-dev}}$ and $F_{\text{std-dev}}$) do not address all variables that impact on the calculations and that further work is needed in this area. The estimates would also need to account for errors associated with the MLR scaling factors.

⁷⁷ Although different temperatures were investigated during 2004, the number of samples was very limited. More co-located sampling would be required to determine a more "correct" temperature setting. Of the data obtained, however, 275°C appeared to provide reasonable estimates.

⁷⁸ The TOR method of analysis is conducted in the US and is not necessarily the most cost-effective method of determining OC and EC concentrations.

studies (e.g. Kim and Hopke, 2003; Kim *et al.*, 2003a; Polissar *et al.*, 2001; Poirot *et al.*, 2001). These methods have been used to determine the conditions under which high concentrations of each source occur. Cluster analysis has also been used to group backward air mass trajectories (e.g. Lee *et al.*, 2002b). These techniques could potentially be applied to the Christchurch data to determine the origin of less certain sources, such as aged aerosol. However, secondary particulate sources, which do not necessarily have constant, unique source compositions, are more difficult to model using trajectory techniques as these usually increase or decrease in response to meteorological influences (Poirot *et al.*, 2001). Also, these techniques can only produce qualitative indications of predominant transport patterns and cannot be validated without using chemical tracers. Nevertheless, this area merits investigation.

Possibly of greatest importance, is the need for a New Zealand based "source library" to provide greater certainty in the identification of resolved factors. A dedicated study, designed to collect source profile data and SEM micrographs of particles present on filters, would be required. The types of sources that need to be characterised include soil, marine aerosol, residential wood burners, residential coal burners, diesel vehicles, petrol vehicles, and various industrial processes. The data collected should not be limited to the elements analysed by PIXE. Marker PAHs and VOCs, as well as formaldehyde and levoglucosan (for residential wood burners), and contaminants that may be targeted in future standards (e.g. benzene and benzo(a)pyrene) would be useful.

While work is needed to further refine receptor modelling in New Zealand, this study has demonstrated that receptor models can be applied successfully to PM_{2.5} data in this country. These valuable tools provide substantial additional source attribution information to that derived from emission inventories and can provide much greater confidence in the appropriateness, and likely success of, air quality strategies. Receptor models have the potential to play a fundamental role in air quality management programmes in areas where air quality is a substantial issue.

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Appendix 1: Field sheet for SuperSASS

Run No:											
START DATE:			END DATE:								
Channel Number	Filter weight before	Filter weight after	Start Time:	End Time:	Event Length:	Pressure	Ambient T (°C)	Total Volume (m³)	Filter T (°C)	Mean Flow (l m ⁻¹)	Max dT (°C)
1											
2											
3											
4											
5											
6											
7											
8											
Warnings: Elapsed Time:											
dT:											
Flow:											
ADDITIONAL COMMENTS:											

Appendix 2: Data transformations and error allocations used in this study

Parameter	Conversion
Field data	On days split into two, event length and total volumes were added together. Ambient pressure, temperature and filter temperature were averaged.
Elemental concentrations	<ol style="list-style-type: none"> 1. Data were checked against limits of detection (LOD). 2. Data were classified as: T = above detection limit F = value given but below detection limit Z = zero data 3. If data = missing then: $x_{ij} = \tilde{v}_{ij}$ Where \tilde{v}_{ij} = geometric mean of the measured concentration (separate values used for summer and winter) were substituted in after replacing "0" data with 1/2 the arithmetic mean detection limit. 4. Measurements on split sample days were added together (ng cm^{-2}). 5. The limit of detection (LOD) values (ng cm^{-2}) for the split sampling days were combined, by averaging the data. These were needed in the data substitutions. 6. Elemental values in ng cm^{-2} converted to $\mu\text{g m}^{-3}$ by: $x_{ij} (\mu\text{g m}^{-3}) = \frac{\left(\frac{x_{ij} (\text{ng cm}^{-2}) * 11.95}{v_{std}} \right)}{1000}$ where x_{ij} = measured concentration v_{std} = standardised volume (see PM_{2.5}) 11.95 = filter area (cm^2)
Elemental errors	<ol style="list-style-type: none"> 1. Fit error values (%) were firstly converted to ng cm^{-2} data $e_{ij} = f_{ij} * x_{ij}$ Where e_{ij} = elemental error f_{ij} = fit error values (%) x_{ij} = concentration values (ng cm^{-2}) 2. If the corresponding concentration values were below detection limits, equal to zero or missing. The adjustments were as follows: Below detection limits: $e_{ij} = u_{ij} + \frac{d_{ij}}{3}$ Equal to zero: $e_{ij} = \frac{d_{ij}^k}{2} + \frac{d_{ij}}{3}$

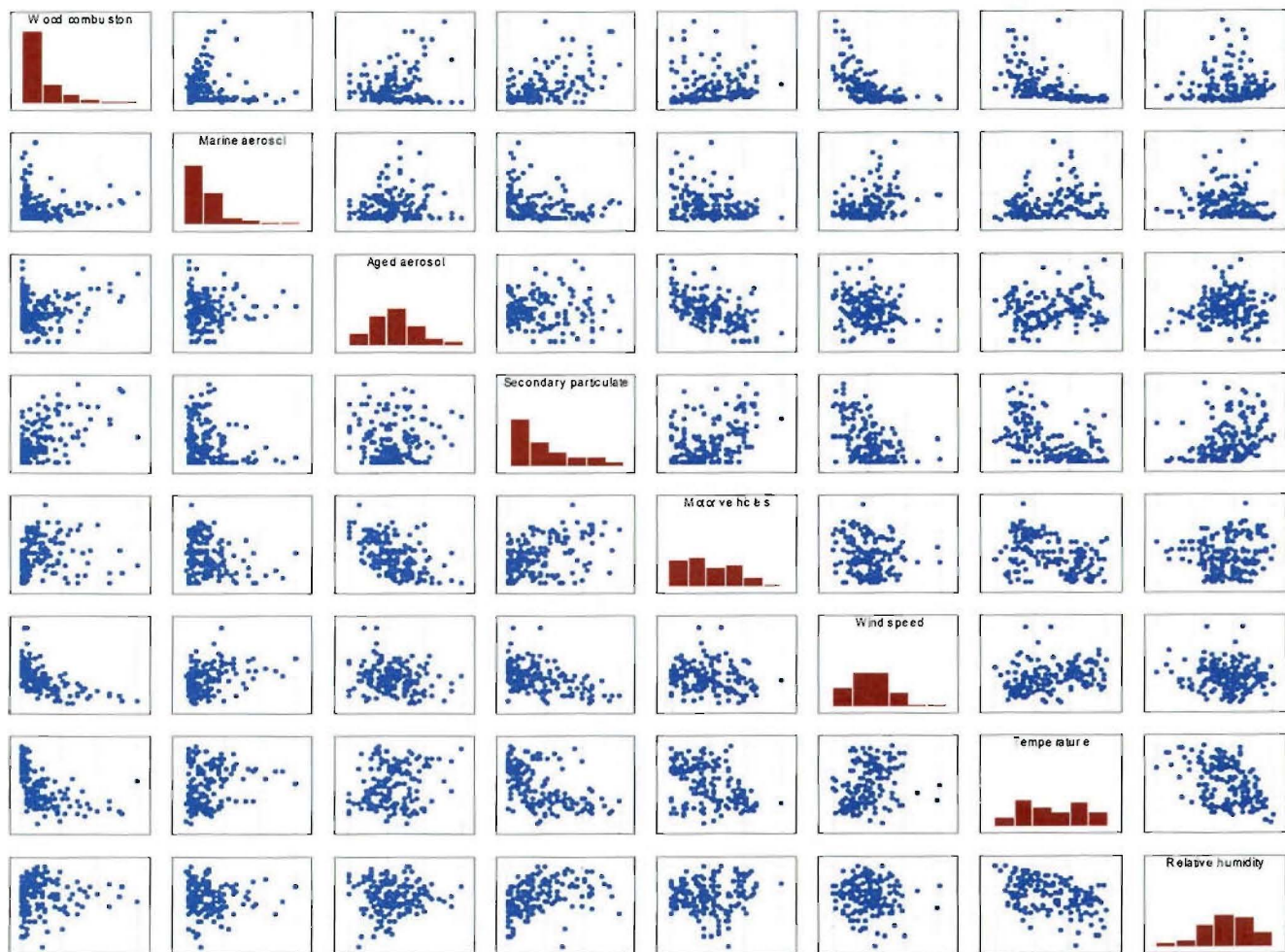
Parameter	Conversion
	<p>Missing values: $e_{ij} = 4\tilde{v}_{ij}$</p> <p>Where e_{ij} = error values</p> <p>u_{ij} = uncertainty estimate (converted fit errors used)</p> <p>d_{ij} = corresponding detection limit value</p> <p>d_{ij}^k = arithmetic mean detection limit</p> <p>\tilde{v}_{ij} = geometric mean of measured concentration</p> <p>3. Fit errors for the classified split sampling days (see Elemental concentrations, point 2) were combined as follows: T + T = values added together T + F = values added together F + F = values added together T + Z = only T value used F + Z = only F value used Z + Z = the values are averaged</p> <p>4. The e_{ij} values were converted to $\mu\text{g m}^{-3}$ by:</p> $\sigma_{ij} = \frac{\left(\frac{e_{ij} * 11.95}{v_{std}} \right)}{1000}$ <p>Where σ_{ij} = error in $\mu\text{g m}^{-3}$</p> <p>e_{ij} = error values (ng cm^{-2})</p> <p>v_{std} = standardised volume (see $\text{PM}_{2.5}$)</p> <p>11.95 = filter area (cm^2)</p> <p>5. Additional error adjustments were made for data that appeared invalid (but no analytical evidence to support removing the data from the analysis), and with greater numbers of samples missing, or generally deemed less reliable than other species.</p> <ul style="list-style-type: none"> ○ Silicon - 30/8/02 error x 2 ○ Aluminium - 7/7/02 error x 2 ○ Sodium - all errors x 2 ○ Zinc - all errors x 2 ○ BC - 24/5/02 x 2
Black carbon	Refer to elemental concentrations and errors.
$\text{PM}_{2.5}$ ($\mu\text{g m}^{-3}$)	<p>1. $M_{2.5} = (M_1 - M_2) * 1 \times 10^6$</p> <p>Where $M_{2.5}$ = total mass (μg) M_1 = filter post-sampling weight (g) M_2 = filter pre-sampling weight (g)</p> <p>2. On days when two samples were collected, the $M_{2.5}$ values were added together.</p>

Parameter	Conversion
	<p>3. $P = P_{\text{mmHg}} * \left(\frac{1}{7.5} \right)$</p> <p>Where P = Pressure in kPa P_{mmHg} = Pressure in mmHg</p> <p>4. $T_k = T_c + 273.15$</p> <p>Where T_k = temperature in kelvin T_c = temperature in degrees centigrade</p> <p>5. Data are required to be reported at conditions of standard temperature and pressure (273.15 K and 101.3 kPa). Volume is corrected to take this into account as follows:</p> $V_{std} = V_m * \left(\left(\frac{273.15}{T_k} \right) * \left(\frac{P}{101.3} \right) \right)$ <p>Where V_{std} = standardised volume in m^3 V_m = volume in m^3 T_k = temperature in kelvin P = pressure in kPa</p> <p>6. $PM_{2.5} = \frac{M_{2.5}}{V_{std}}$</p> <p>Where $PM_{2.5}$ = particle concentration in $\mu\text{g m}^{-3}$ $M_{2.5}$ = total mass (μg) V_{std} = standardised volume (m^3)</p> <p>Data were assessed against the LOD and values were substituted where required in accordance with the criteria outlined under elemental concentrations.</p> <p>$PM_{2.5}$ was not included in the receptor modelling and error estimates were not required.</p>
Inorganic ion (concentration)	<p>1. Ion concentrations were obtained for ammonia nitrogen, chloride, nitrate nitrogen and sulphate ($\mu\text{g filter}^{-1}$). Ammonia nitrogen was converted to ammonium by:</p> $\frac{NH_4N * 18}{14}$ <p>Nitrate nitrogen was converted to nitrate by:</p> $\frac{NO_3N * 62}{14}$ <p>2. The concentrations of the ions in $\mu\text{g m}^{-3}$ were calculated as follows:</p> $I_{ij} = \frac{IC_{ij}}{V_{std}}$ <p>Where I_{ij} = ion concentration ($\mu\text{g m}^{-3}$)</p>

Parameter	Conversion
	IC_{ij} = ion mass ($\mu\text{g filter}^{-1}$) v_{std} = standardised volume (see PM _{2.5}) 3. Data were assessed against the LOD provided by the laboratory and values were substituted where required in accordance with the criteria outlined under elemental concentrations.
Inorganic ion (error)	The errors were based on the 95% confidence limit values provided by the analytical laboratory. Values were substituted where required in accordance with the criteria outlined under elemental errors. The exception is ammonium. When the elemental error criteria were applied greater weighting was actually given to below detection limit data than those above detection limits. The detection limit value for ammonium was multiplied by 5% to ensure that this did not occur. 6. Additional error adjustments were made for data that appeared invalid (but no analytical evidence to support removing the data from the analysis), and with greater numbers of samples missing, or generally deemed less reliable than other species. <ul style="list-style-type: none"> ○ Nitrate – 20/6/02 error x 10, all other errors x 3 ○ Ammonium – all errors x 2
OC (concentration)	The original values provided ($\mu\text{g m}^{-3}$) were adjusted to take into account oxygen and hydrogen: $OC_{mass} = \text{total OC } (\mu\text{g m}^{-3}) * 1.4^{79}$ Data were assessed against the LOD and values were substituted where required in accordance with the criteria outlined under elemental concentrations.
OC (error)	Based on the measurement resolution of the instrument ($0.25 \mu\text{g m}^{-3}$) and multiplied by 1.4 as above. Values were substituted where required in accordance with the criteria outlined under elemental concentrations. Additional error adjustments were made for data that appeared invalid (but no analytical evidence to support removing the data from the analysis), and with greater numbers of samples missing, or generally deemed less reliable than other species. <ul style="list-style-type: none"> ○ OC – 5/7/02 x 5, 14/6/02 x 5 ○ EC – 5/7/02 x 5, 14/6/02 x 5
EC (error)	Based on the measurement resolution of the instrument ($0.25 \mu\text{g m}^{-3}$). Values were substituted where required in accordance with the criteria outlined under elemental errors. Additional error adjustments were made for data that appeared invalid (but no analytical evidence to support removing the data from the analysis), and with greater numbers of samples missing, or generally deemed less reliable than other species.

⁷⁹ This is a fairly standard aerosol conversion. The equation may be referenced at <http://vista.circa.colostate.edu/improve/Tools/AerTypeEqs.htm>

Appendix 3: Scatterplots of the G-factors and various meteorological variables, Christchurch, 2001/2002

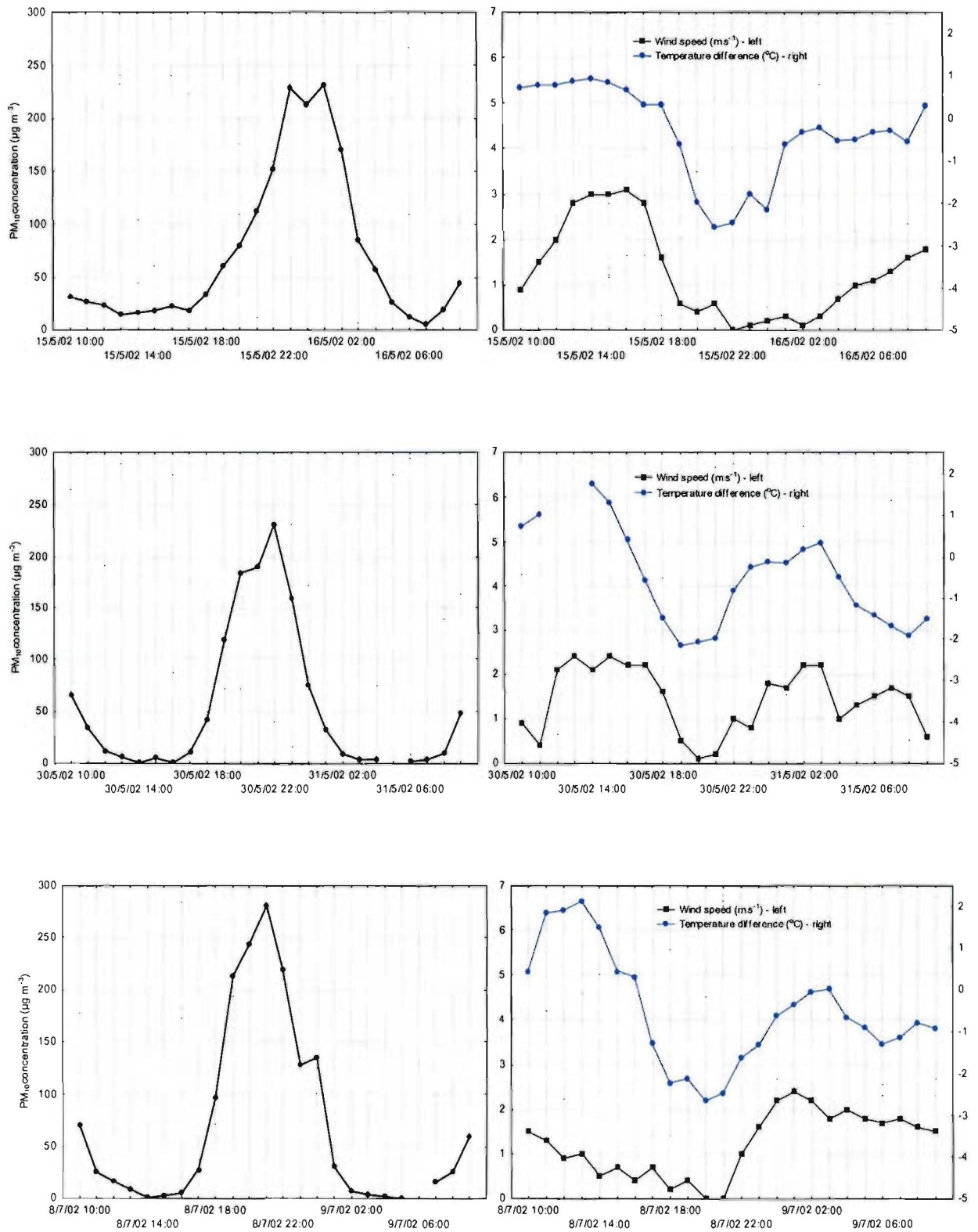


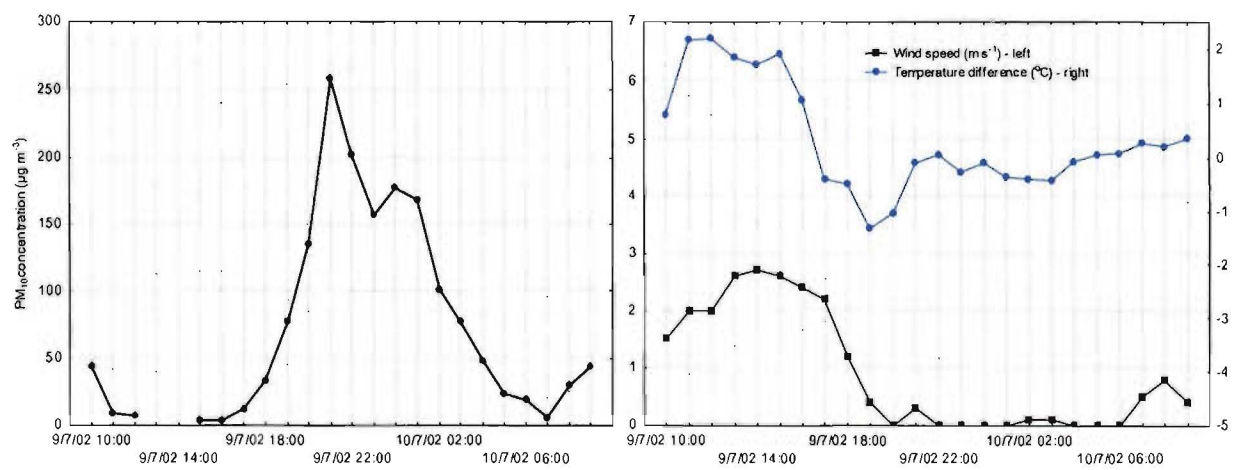
**Appendix 4: Spearman Rank correlation analysis of
daily source contributions and meteorological
variables, Christchurch, 2001/2002**

Total dataset	Wood combustion	Marine aerosol	Aged aerosol	Secondary particulate	Motor vehicles	Wind speed	Temperature	Relative humidity
Wood combustion	1							
Marine aerosol	-0.1	1						
Aged aerosol	0.01	-0.01	1					
Secondary particulate	0.54	-0.3	-0.04	1				
Motor vehicles	0.35	-0.18	-0.54	0.36	1			
Wind speed	-0.65	0.3	-0.17	-0.49	-0.21	1		
Temperature	-0.77	0.1	0.17	-0.55	-0.36	0.39	1	
Relative humidity	0.17	-0.24	0	0.42	0.09	-0.1	-0.42	1
Summer	Wood combustion	Marine aerosol	Aged aerosol	Secondary particulate	Motor vehicles	Wind speed	Temperature	Relative humidity
Wood combustion	1							
Marine aerosol	0.19	1						
Aged aerosol	-0.11	-0.08	1					
Secondary particulate	-0.33	-0.47	0.44	1				
Motor vehicles	0.1	-0.09	-0.52	-0.27	1			
Wind speed	-0.35	0.4	-0.08	-0.21	-0.03	1		
Temperature	-0.29	-0.32	0.08	0.2	0.16	0.05	1	
Relative humidity	-0.11	-0.04	0.3	0.4	-0.36	0.04	-0.34	1
Winter	Wood combustion	Marine aerosol	Aged aerosol	Secondary particulate	Motor vehicles	Wind speed	Temperature	Relative humidity
Wood combustion	1							
Marine aerosol	0.03	1						
Aged aerosol	0.54	-0.03	1					
Secondary particulate	0.41	-0.06	-0.1	1				
Motor vehicles	-0.24	-0.13	-0.52	0.33	1			
Wind speed	-0.72	0.1	-0.4	-0.48	-0.02	1		
Temperature	-0.32	0	-0.05	-0.41	0.03	0.15	1	
Relative humidity	-0.22	-0.35	-0.06	0.27	0.07	0.07	-0.24	1

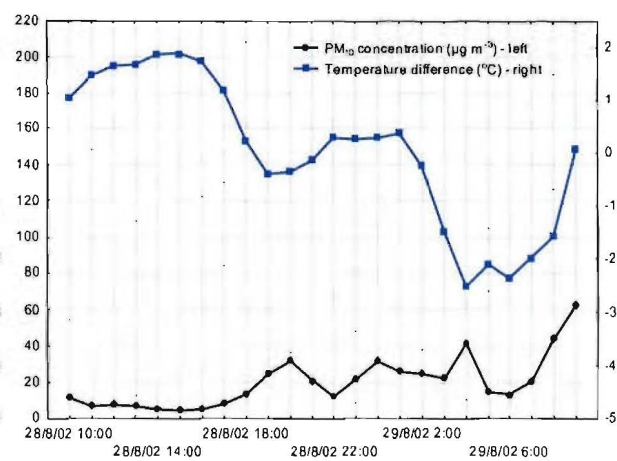
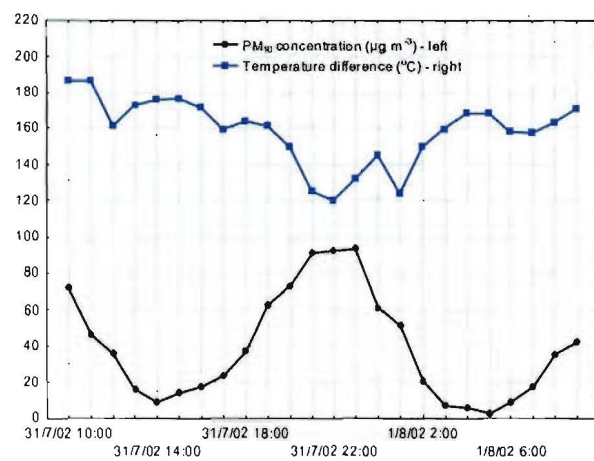
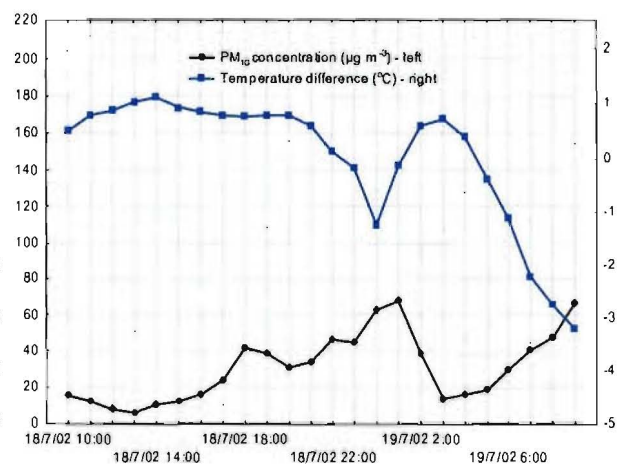
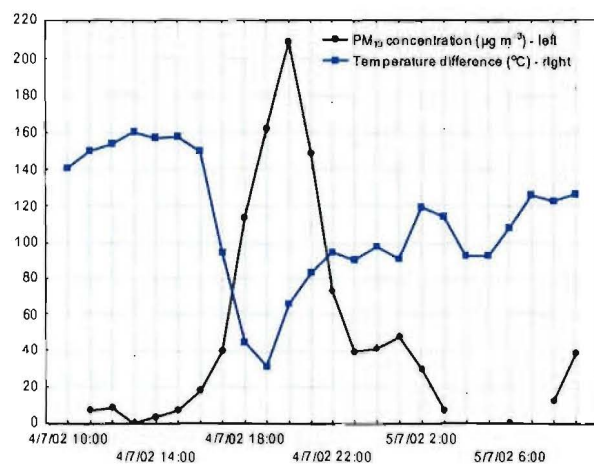
NB: Coefficients greater than 0.7 are highlighted in bold.

**Appendix 5 – Hourly PM₁₀ concentrations, wind speed
and temperature difference on four peak wood
combustion contribution days, St Albans,
Christchurch**

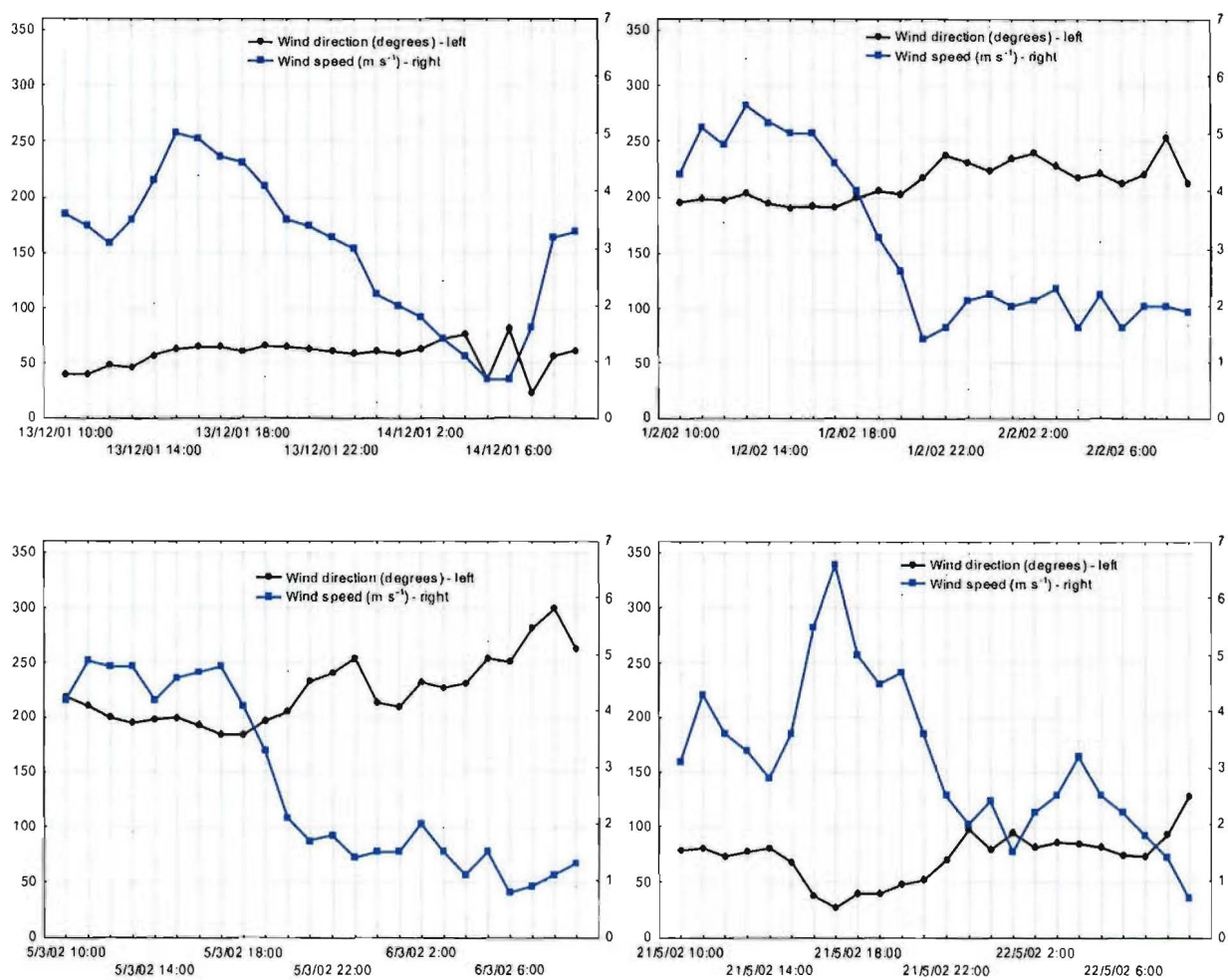




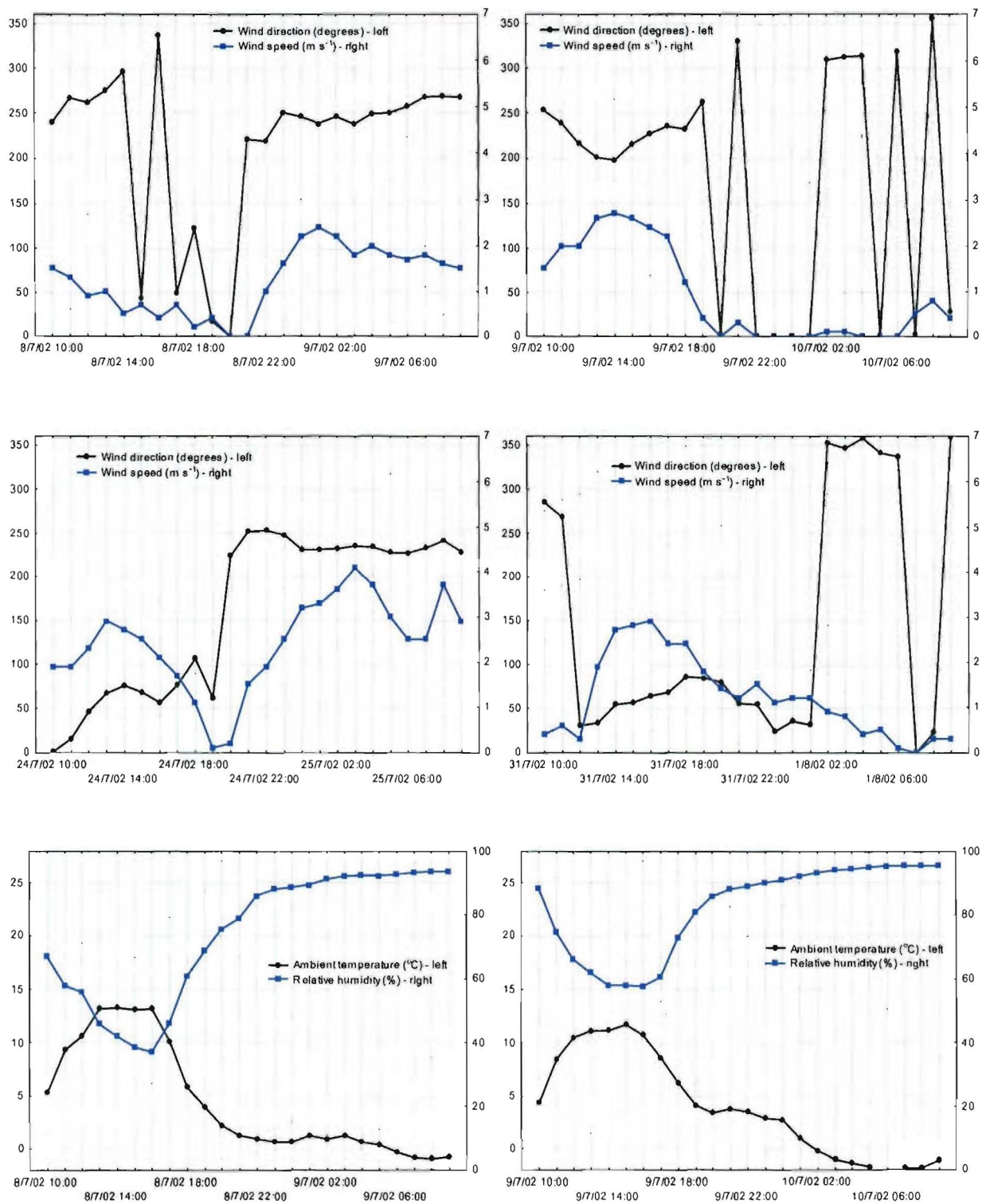
Appendix 6: Hourly PM₁₀ concentrations and temperature difference on four peak motor vehicle contribution days, St Albans, Christchurch

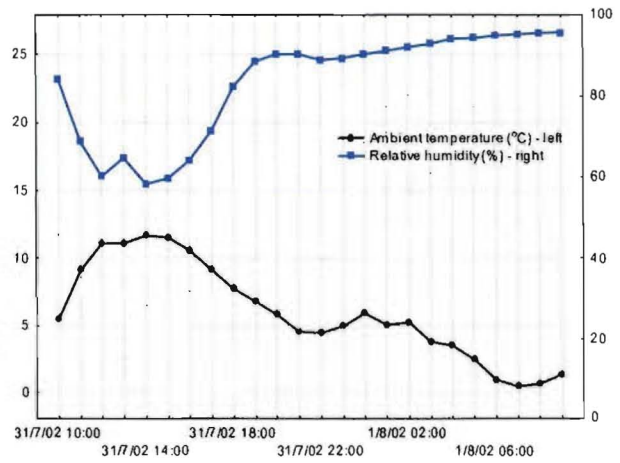
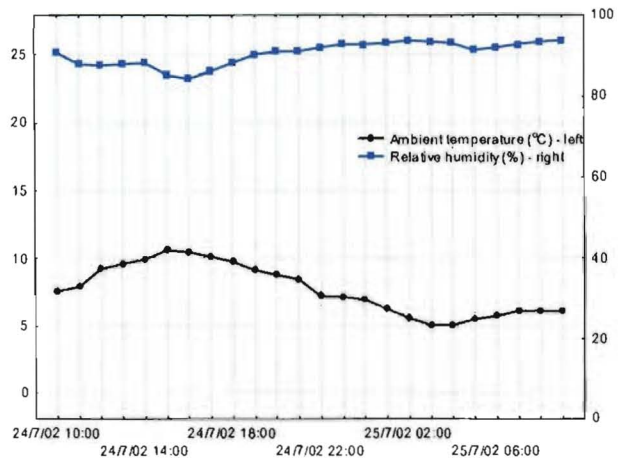


**Appendix 7: Hourly wind speed and direction on four
peak marine aerosol contribution days, St Albans,
Christchurch**

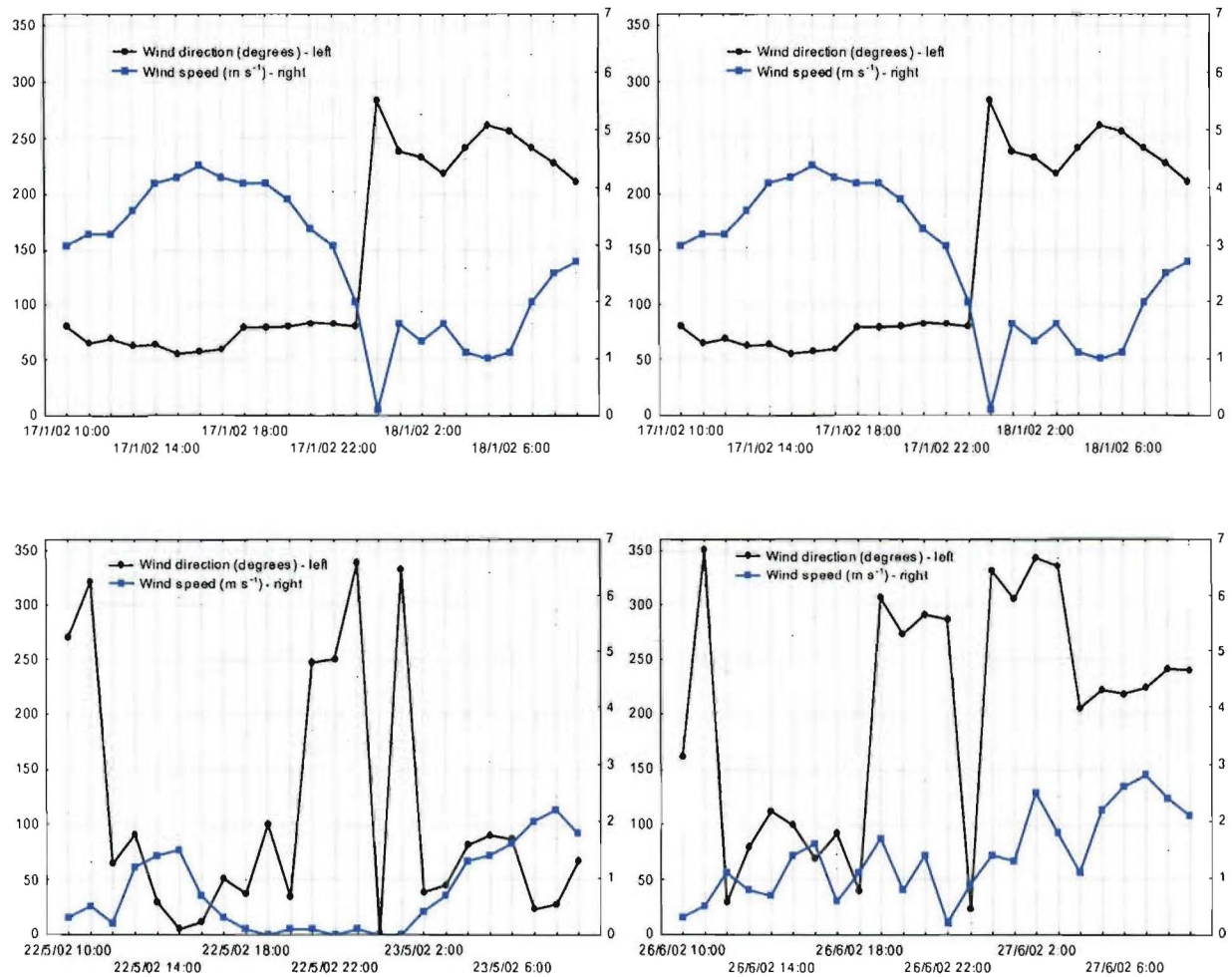


**Appendix 8: Hourly wind speed and direction,
ambient temperature and relative humidity on four
peak secondary particulate contribution days, St
Albans, Christchurch**

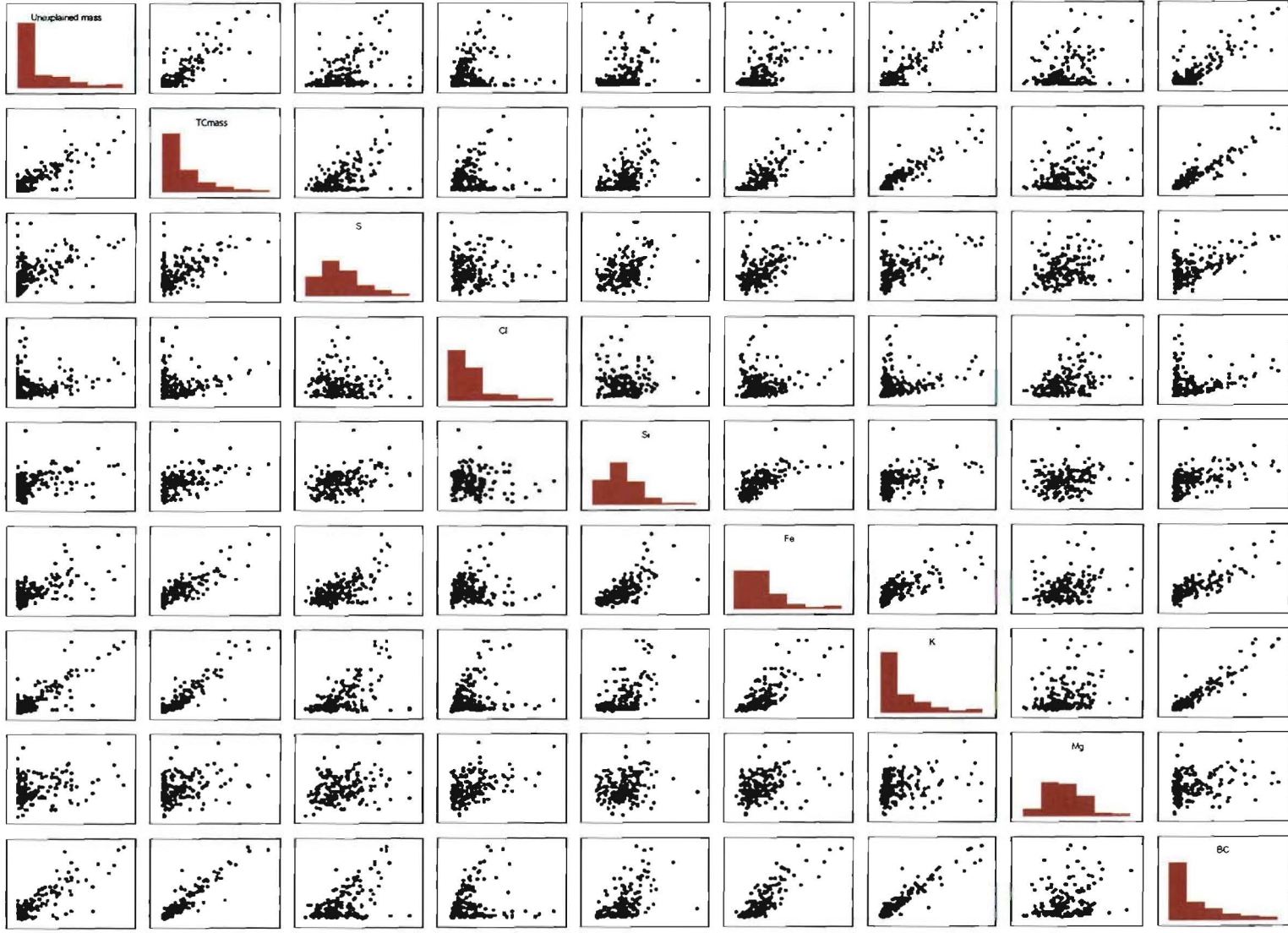


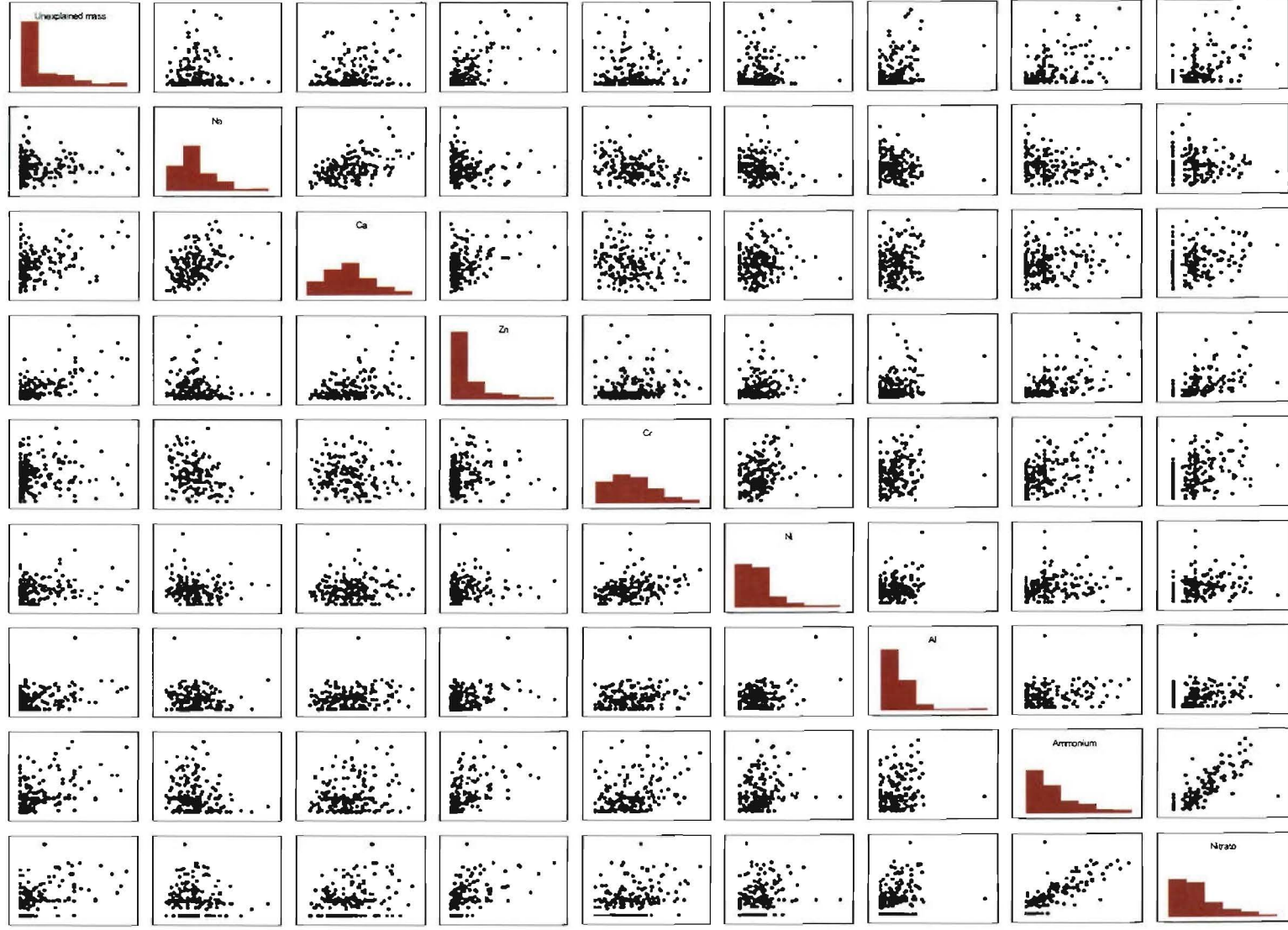


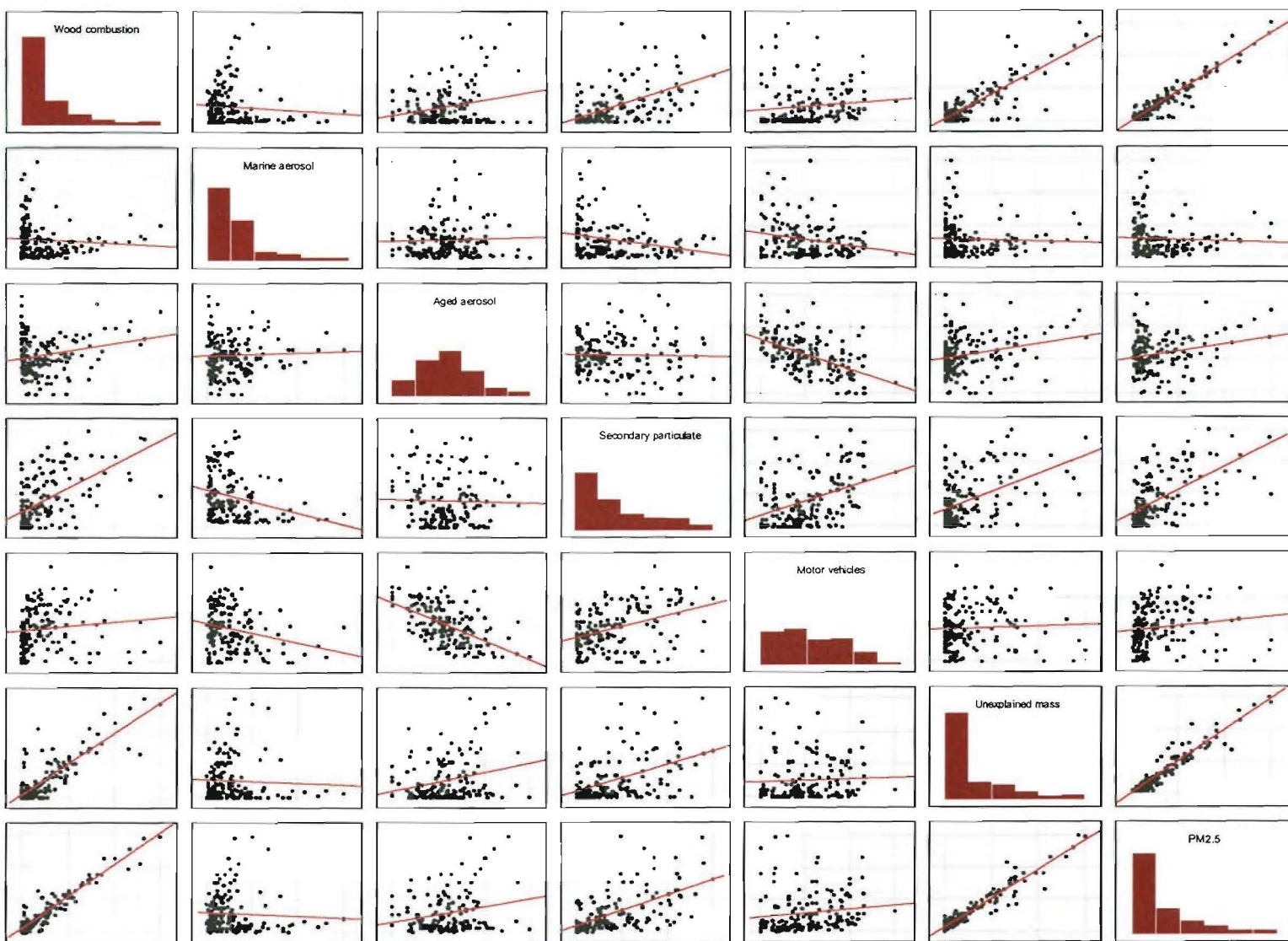
**Appendix 9: Hourly wind speed and direction on
four peak aged aerosol contribution days, St
Albans, Christchurch**



Appendix 10: Matrix plots including unexplained mass contributions, Christchurch, 2001/2002







Appendix 11: Suggested source apportionment programme

Programme Duration: For each location of concern, monitoring should be conducted for at least one year at three-yearly intervals. Ideally this would be timed to coincide with other source attribution work such as emission inventories and/or any plan monitoring requirements.

Site Location: Where a long-term monitoring site is available, i.e. used for establishing trends and for comparing concentrations with guidelines and standards, this should be used. Also, monitoring should be conducted in close proximity to routine sampling of contaminant concentrations and of meteorological variables (wind speed and direction, temperature and temperature difference).

Sampling Regime: 24-hour samples, every second day for one year (at least). Duplicate samples should be collected once a week, in the first year of sampling at a site, to assist in determining sample uncertainties.

Instrumentation/Analytical Methods: Sequential samplers such as the SuperSASS are highly recommended as they are simple to use and multiple samples may be collected. However, this sampler is not an EPA reference method for the collection of PM_{2.5} and it may be advisable to source a speciation sampler that is a reference method or designated equivalence. In addition, there were issues with high particulate loads and filter blockages can occur and while changing the filter substrate will partially address this issue it may be worth investigating whether there are other samplers available that are designed to avoid this problem. For example, Core (1991) described a sampler used in the Oregon sampling programme that will transfer sampling to another set of filters when the pressure drop across the filter drops below a certain point. Ringed Teflon filters are recommended for the collection of PM for gravimetric mass and elemental analysis by PIXE. It is also useful to obtain SEM micrographs of key filters for analysis to assist with source characterisation. If carbon denuders are available then collection of PM for OC and EC analysis may be conducted using a single quartz-fibre filter. Otherwise, dual sampling such as that conducted during this study is advisable. Sampling of inorganic ions should be similar to that employed during this study with a MgO denuder followed by hydrophilic Teflon and nylon filters in tandem. The Teflon and nylon filters should be analysed separately using IC. The Teflon filter may be analysed for nitrate, sulphate, sodium, chloride, ammonium and potassium, and the nylon filters for nitrate only.

Receptor modelling and source apportionment: The PMF receptor model provided an excellent characterisation of the main sources contributing to PM_{2.5} in Christchurch. However, preparing the error matrix can be time consuming and it may be useful to evaluate whether other receptor models such as UNMIX can also provide good source apportionment. Nevertheless, regardless of the receptor model used, the results must be carefully evaluated to determine whether the sources are correctly identified, and how much of the PM mass can be explained by the elemental species

measured and by the resolved sources. Also required, is calculation of the uncertainties associated with the estimated source contributions. The PMF receptor model presently provides uncertainty estimates for the G and F-Factors. However, Pentti Paatero (*pers. comm.*, Helsinki, Finland) indicates that these estimates (G_std-dev and F_std-dev) do not address all variables that impact on the calculations and that further work is needed in this area. The estimates would also need to account for errors associated with the MLR scaling factors.

Source reconciliation: The results obtained by the receptor model should be evaluated against modelled emission inventory data. The emissions data needs to be transformed into concentrations using airshed models to verify whether or not the two methods provide similar results. If not, then there may be issues associated with the emission inventory, the airshed model or the receptor modelling that may need to be addressed. This should be investigated, uncertainties reduced, and methodologies improved.

The final steps involve writing up and publishing the research. This is essential to provide greater certainty to regulators and the community regarding the sources identified and provide greater confidence that air quality strategies will lead to reductions in PM.